Abstract

A chemistry procedure is developed for the Sudbury Neutrino Observatory (SNO) to determine the ^{232}Th Neutral Current background via the assay of ^{212}Pb at 10% of the $3 \times 10^{-15} \text{ g}(^{232}\text{Th})/\text{g}(\text{D}_2\text{O})$ level as objective. After the Standard Solar Model (SSM), the Solar Neutrino Problem (SNP) and various proposed solutions, and past and future neutrino experiments including SNO are discussed, the development of the three stages of the chemistry procedure is reviewed. The three stages are the preconcentration of a large water sample (1 tonne or more) down to 360 cc's by Reverse Osmosis, the elution and separation of ^{212}Pb from the complexing agent EthylenediamineTetraacetic Acid (EDTA), the PbCl_2 precipitation of the few atoms of ^{212}Pb along with 0.1 mg of stable lead carrier as PbCrO_4 , and the α spectrometer used to detect the α particles from the decay of the ^{212}Po and ^{212}Bi daughters. The stable lead carrier recovery efficiency of the technique is shown to be $\sim 64\%$ overall with an added 25% geometric efficiency whereas the blank level found was $(570 \pm 520) \text{ cpl}$ for two stages of Reverse Osmosis. The most probable sources of contamination which give rise to the high blank level are the RO system and membrane and the ^{212}Pb source making apparatus. The ultimate sensitivity achieved was $(10.1 \pm 9.2) \times 10^{-12} \text{ g}(^{232}\text{Th})/\text{g}(\text{UltrapureWater})$ far short of the $3 \times 10^{-16} \text{ g/g}$ desired.

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395 rue Wellington
Ottawa (Ontario)
K1A 0N4

Your library's microfilm

Quelle est votre microforme

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

**^{212}Pb Assay For The Determination of The
Neutral Current Background at The Sudbury
Neutrino Observatory.**

by

Gaëtan Laberge B.Sc., M.Sc.

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of the requirements
for the degree of
Master of Science

Ottawa-Carleton Institute for Physics
Department of Physics, Carleton University
Ottawa, Ontario, Canada

July, 1995

©copyright 1995

Gaëtan Laberge

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Your file Votre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-09008-6

Canada

Name William L. Hergert

Dissertation Abstracts International is arranged by broad, general subject categories. Please select the one subject which most nearly describes the content of your dissertation. Enter the corresponding four digit code in the spaces provided.

0779

SUBJECT TERM

0779

SUBJECT CODE

U·M·I

Subject Categories

THE HUMANITIES AND SOCIAL SCIENCES

COMMUNICATIONS AND THE ARTS

Architecture 0729
Art History 0327
Cinema 0906
Dance 0378
Fine Arts 0357
Information Science 0723
Journalism 0391
Library Science 0399
Mass Communications 0708
Music 0413
Speech Communication 0459
Theater 0465

EDUCATION

General 0515
Administration 0514
Adult and Continuing 0516
Agricultural 0517
Art 0273
Bilingual and Multicultural 0282
Business 0688
Community College 0275
Curriculum and Instruction 0727
Early Childhood 0518
Elementary 0524
Finance 0277
Guidance and Counseling 0519
Health 0680
Higher 0745
History of 0520
Home Economics 0278
Industrial 0521
Language and Literature 0279
Mathematics 0280
Music 0522
Philosophy of 0998
Physical 0523

Psychology 0525
Reading 0535
Religious 0527
Sciences 0714
Secondary 0533
Social Sciences 0534
Sociology of 0340
Special 0529
Teacher Training 0530
Technology 0710
Tests and Measurements 0288
Vocational 0747

LANGUAGE, LITERATURE AND LINGUISTICS

Language
General 0679
Ancient 0289
Linguistics 0290
Modern 0291
Literature
General 0461
Classical 0294
Comparative 0295
Medieval 0297
Modern 0298
African 0316
American 0501
Asian 0305
Canadian (English) 0352
Canadian (French) 0355
English 0509
Germanic 0311
Latin American 0312
Middle Eastern 0315
Romance 0313
Slavic and East European 0314

PHILOSOPHY, RELIGION AND THEOLOGY

Philosophy 0422
Religion
General 0318
Biblical Studies 0321
Clergy 0319
History of 0320
Philosophy of 0322
Theology 0469

SOCIAL SCIENCES

American Studies 0323
Anthropology
Archaeology 0324
Cultural 0326
Physical 0327
Business Administration
General 0310
Accounting 0272
Banking 0770
Management 0454
Marketing 0338
Canadian Studies 0385
Economics
General 0501
Agricultural 0503
Commerce Business 0505
Finance 0508
History 0509
Labor 0510
Theory 0511
Folklore 0358
Geography 0366
Gerontology 0351
History
General 0578

Ancient 0579
Medieval 0581
Modern 0582
Black 0328
African 0331
Asia, Australia and Oceania 0332
Canadian 0334
European 0335
Latin American 0336
Middle Eastern 0337
United States 0337
History of Science 0585
Law 0398
Political Science
General 0615
International Law and Relations 0616
Public Administration 0617
Recreation 0814
Social Work 0452
Sociology
General 0626
Criminology and Penology 0627
Demography 0938
Ethnic and Racial Studies 0631
Individual and Family Studies 0628
Industrial and Labor Relations 0629
Public or Social Welfare 0630
Social Structure and Development 0700
Theory and Methods 0344
Transportation 0709
Urban and Regional Planning 0999
Women's Studies 0453

THE SCIENCES AND ENGINEERING

BIOLOGICAL SCIENCES

Agriculture
General 0473
Agronomy 0285
Animal Culture and Nutrition 0475
Animal Pathology 0476
Food Science and Technology 0359
Forestry and Wildlife 0478
Plant Culture 0479
Plant Pathology 0480
Plant Physiology 0817
Range Management 0777
Wood Technology 0746
Biology
General 0306
Anatomy 0287
Biostatistics 0308
Botany 0309
Cell 0329
Ecology 0329
Entomology 0353
Genetics 0369
Limnology 0793
Microbiology 0410
Molecular 0307
Neuroscience 0317
Oceanography 0416
Physiology 0433
Radiation 0821
Veterinary Science 0778
Zoology 0472
Biophysics
General 0786
Medical 0760

EARTH SCIENCES

Biogeochemistry 0425
Geochemistry 0996

Geodesy 0370
Geology 0372
Geophysics 0473
Hydrology 0388
Mineralogy 0411
Paleobotany 0345
Paleoecology 0426
Paleontology 0418
Paleozoology 0985
Palynology 0427
Physical Geography 0368
Physical Oceanography 0415

HEALTH AND ENVIRONMENTAL SCIENCES

Environmental Sciences 0768
Health Sciences
General 0566
Audiology 0300
Chemotherapy 0992
Dentistry 0567
Education 0350
Hospital Management 0769
Human Development 0758
Immunology 0982
Medicine and Surgery 0564
Mental Health 0347
Nursing 0569
Nutrition 0570
Obstetrics and Gynecology 0380
Occupational Health and Therapy 0354
Ophthalmology 0381
Pathology 0571
Pharmacology 0419
Pharmacy 0572
Physical Therapy 0382
Public Health 0573
Radiology 0574
Recreation 0575

Speech Pathology 0460
Toxicology 0383
Home Economics 0386

PHYSICAL SCIENCES

Pure Sciences
Chemistry
General 0485
Agricultural 0749
Analytical 0486
Biochemistry 0487
Inorganic 0488
Nuclear 0738
Organic 0490
Pharmaceutical 0491
Physical 0494
Polymer 0495
Radiation 0754
Mathematics 0406
Physics
General 0605
Acoustics 0986
Astronomy and Astrophysics 0606
Atmospheric Science 0608
Atomic 0748
Electronics and Electricity 0607
Elementary Particles and High Energy 0798
Fluid and Plasma 0759
Molecular 0609
Nuclear 0610
Optics 0752
Radiation 0756
Solid State 0611
Statistics 0463
Applied Sciences
Applied Mechanics 0346
Computer Science 0984

Engineering
General 0537
Aerospace 0538
Agricultural 0539
Automotive 0540
Biomedical 0541
Chemical 0542
Civil 0543
Electronics and Electrical 0544
Heat and Thermodynamics 0348
Hydraulic 0545
Industrial 0546
Marine 0547
Materials Science 0794
Mechanical 0548
Metallurgy 0743
Mining 0551
Nuclear 0552
Packaging 0549
Petroleum 0765
Sanitary and Municipal System Science 0554
System Science 0790
Geotechnology 0428
Operations Research 0796
Plastics Technology 0795
Textile Technology 0994

PSYCHOLOGY

General 0621
Behavioral 0384
Clinical 0622
Developmental 0620
Experimental 0623
Industrial 0624
Personality 0625
Physiological 0989
Psychobiology 0349
Psychometrics 0632
Social 0451

The undersigned recommend to the Faculty of Graduate Studies
and Research acceptance of this thesis

**^{212}Pb ASSAY FOR THE DETERMINATION OF THE
NEUTRAL CURRENT BACKGROUND AT THE SUDBURY
NEUTRINO OBSERVATORY**

submitted by Gaëtan Laberge, B.Sc., M.Sc.

in partial fulfilment of the requirements
for the degree of Master of Science

Thesis Supervisor

Chair, Department of Physics

Carleton University

Date: 31.8.95

Abstract

A chemistry procedure is developed for the Sudbury Neutrino Observatory (SNO) to determine the ^{232}Th Neutral Current background via the assay of ^{212}Pb at 10% of the $3 \times 10^{-15} \text{ g}(^{232}\text{Th})/\text{g}(\text{D}_2\text{O})$ level as objective. After the Standard Solar Model (SSM), the Solar Neutrino Problem (SNP) and various proposed solutions, and past and future neutrino experiments including SNO are discussed, the development of the three stages of the chemistry procedure is reviewed. The three stages are the preconcentration of a large water sample (1 tonne or more) down to 360 cc's by Reverse Osmosis, the elution and separation of ^{212}Pb from the complexing agent EthyleneDiamineTetraacetic Acid (EDTA), the final precipitation of the few atoms of ^{212}Pb along with 0.1 mg of stable lead carrier as PbCrO_4 , and the α spectrometer used to detect the α particles from the decay of the ^{212}Po and ^{212}Bi daughters. The stable lead carrier recovery efficiency of the technique is shown to be $\sim 64\%$ overall with an added 25% geometric efficiency whereas the blank level found was (570 ± 520) cpd for two stages of Reverse Osmosis. The most probable sources of contamination which give rise to the high blank level are the RO system and membrane and the ^{212}Pb source making apparatus. The ultimate sensitivity achieved was $(10.4 \pm 9.2) \times 10^{-12} \text{ g}(^{232}\text{Th})/\text{g}(\text{Ultrapure Water})$ far short of the $3 \times 10^{-16} \text{ g/g}$ desired.

Acknowledgements

I wish to thank all those who have given me invaluable help and guidance throughout the past several years. Michal Shatkay, Cathy Shewchuk, and Muiyi Chen who so graciously tolerated the daily presence of a Physics Major in their chemistry laboratory deserve the greatest of thankyou's above and beyond what is owed to them for their help. I would also like to thank David Sinclair in particular and the Ottawa-Carleton Institute for Physics for their help and financial support. Last but definitely not least are my two children, Jeanne d'Arc and Moïse, and my understanding wife Nathalie who had to endure my absence for several months.

May The Force be With You

Contents

Acceptance sheet	ii
Abstract	iii
Acknowledgements	v
1 Introduction	1
2 The Solar Neutrino Problem	8
2.1 Precis of The Standard Solar Model	8
2.2 The First Solar Neutrino Experiment	17
2.3 The Birth of The Solar Neutrino Problem	19
2.4 Subsequent Solar Neutrino Experiments	21
2.4.1 Kamiokande II & III	21
2.4.2 SAGE	22
2.4.3 Gallex	24
2.5 Some proposed Solutions to The Solar Neutrino Problem	27
2.5.1 Non-Standard Solar Models	27
2.5.2 Vacuum Neutrino Flavour Oscillations	29
2.5.3 Matter Induced Neutrino Oscillations	31
2.5.4 MSW Neutrino Flux Regeneration at Earth	34
2.5.5 Neutrino Magnetic Moments	35
2.5.6 Neutrino Decay	37
2.6 SM Implications of ν Oscillations	37

2.7	SSM Versus Physics Based SNP Solutions and Experimental Results	39
2.8	Future Solar Neutrino Experiments	43
2.8.1	Super-Kamiokande	43
2.8.2	Borexino	46
3	The Sudbury Neutrino Observatory (SNO)	50
3.1	What SNO Proposes to Measure and Why	50
3.2	The SNO Detector Design	56
3.2.1	The Structure of The Detector	56
3.2.2	Sources of Internal and External Backgrounds	61
3.3	The Importance of Pure Light and Heavy Water	67
3.4	The Assay of Th and U Chains via Radon	69
3.5	The Heavy Water Purification System	73
4	Lead Monitoring for The Heavy Water Purification System	81
4.1	The Need for The Assay of Th via ^{212}Pb	81
4.2	The Alpha Spectrometer	85
4.3	^{212}Pb Calibration Sources and Spikes.	90
4.4	Precipitation	92
4.5	Elution	111
4.6	Reverse Osmosis	122
4.7	Synopsis of All Results	140
5	Conclusion	143
5.1	A Comparison of The Various Assay Techniques Developed for SNO.	143
5.2	Conclusion	147

List of Tables

2.1	Neutrino flux contributions from all p-p and some CNO chain reactions for 8 different target nuclei of interest.	20
2.2	The main fundamental constituents of the SM.	38
2.3	Current solar- ν detector results: measured rates, neutrino type, expected rate, and different contribution sources for the expected rate.	40
3.1	The expected solar ν signal rates in SNO for various ν reactions. . .	52
3.2	The desired levels of ^{232}Th and ^{238}U for various detector components in grams per gram of material.	65
4.1	Stable lead carrier recovery (determined gravimetrically) as a function of pH.	98
4.2	Gravimetric and FAA stable lead carrier recovery results.	103
4.3	Alpha spectrometer data for several blank runs.	110
4.4	Amount of EDTA eluted per aliquot of eluant for a 5:1 EDTA:Pb spike test.	114
4.5	Amount of stable lead carrier eluted per aliquot of the various eluants during a trial elution.	115
4.6	Stable lead recovery by FAA analysis for the elution procedure for 5:1 and 100:1 EDTA:Pb mass ratios.	116
4.7	Stable lead recovery, full procedural blank, and ^{212}Pb source tests of the elution and precipitation procedures combined.	119

4.8	Typical operating parameters for the operation of the 'TRO systems' first and second stage.	131
4.9	Listed is the relevant α data for several blank and split source spike runs on the TRO system.	133
4.10	^{212}Pb assay technique parameters.	141
5.1	A comparison of the parameters which define the assay techniques which may be used at SNO.	144

List of Figures

2.1	Diagrammatical representation of the p-p chain for the energy generation process in main-sequence stars.	11
2.2	Diagrammatical representation of the CNO cycle for the 1.5% energy generation in the Sun.	12
2.3	Schematic of various solar ν flux versus solar radius.	15
2.4	Various solar ν flux versus ν energy.	16
2.5	MS plot of Δm^2 vs. $\sin^2(2\theta_\nu)$ for all published detectors to date. . .	44
3.1	The Mark II design of the Sudbury Neutrino Observatory detector.	58
3.2	The ^{232}Th decay chain.	63
3.3	The ^{238}U decay chain.	64
3.4	The Heavy Water Purification System for SNO.	75
4.1	Long term background data for the dual chamber alpha spectrometer.	89
4.2	pH curve for the precipitation procedure.	99
4.3	Electron Microscope photographs of the PbCrO_4 precipitate.	102
4.4	Example of airborne ^{212}Pb activity in fumehood.	106
4.5	Split ^{212}Pb source data for runs E1A4 and E1B4.	123
4.6	Split ^{212}Pb source data for runs E1A5 and E1B5.	124
4.7	Split ^{212}Pb source data for runs E1A6 and E1B6.	125
4.8	Diagram of the two stage reverse osmosis test system employed for the lead assay technique.	128

4.9	Split ^{212}Pb source data for runs E1A7 and E1B7.	139
------------	---	------------

Chapter 1

Introduction

A new field of astrophysics was born when Ray Davis Jr. set out in the early 1960's to measure the flux of ^8B neutrinos that were theorized to be streaming from the Sun by Bethe and many others afterwards. What was unexpected and surprising was the lack of neutrinos detected in comparison to that predicted by what is known as the Standard Solar Model, hence the Solar Neutrino Problem was coined. Many modifications, corrections, and improvements were subsequently made to the solar model, which had become a computerized model by the 1960's, incorporating many physical and nuclear processes in an attempt to derive (as opposed to measuring) most of the known solar parameters. Despite all the improvements to the model, all the predictions remained to within 10% of each other. Several more experiments, such as SAGE, GALLEX, and the Kamioka Nucleon Decay Experiment (Kamiokande), were initiated in order to shed more light on the problem of the missing neutrinos. Although some progress was made, as with all research, more questions were raised than answered. The stage was therefore set for a new generation of experiments which would employ different target materials.

The Sudbury Neutrino Observatory (SNO) was to be one of these next generation neutrino detectors. Situated deep underground (2 km) for protection against muon induced background signals, the SNO detector consists of a novel 1000 tonnes

of heavy water as primary target material whose acrylic containment vessel bathes in 7500 tonnes of light water. Although all other detectors, with the exception of Kamiokande, have considerably lower energy thresholds (0.2 to 0.9 MeV) compared to the 6 MeV of SNO (7.5 MeV for Kamiokande), SNO nevertheless has a distinct advantage. Because of the nature of the two different reactions employed by Homestake (Davis et al), SAGE and GALLEX, they could only 'see' electron neutrinos. Neutrinos, as outlined in Electroweak theory, come in three flavors; electron, muon, and tau. Kamiokande could also effectively (because of the much lower rate for muon or tau neutrinos) only 'see' neutrinos of the electron flavour because only light water was used as target material. SNO, on the other hand, has a flavour blind capability. As with Kamiokande, an electron neutrino signal from elastic scattering on the electrons in the light and heavy water is available. The added bonus, so to speak, stems from the alternate use of heavy water. Two interactions are possible: a charged current (CC) one where the electron neutrino transforms the neutron (in the deuterium nucleus) into a proton releasing an electron (thus destroying the deuteron as well), and a neutral current reaction (NC) wherein a neutrino of any flavour dissociates the deuterium nucleus into its constituent proton and neutron. Despite the higher energy threshold, the advantage afforded by SNO is clear: the first measurement of the flavour blind solar neutrino flux. It is very important that such a flux be measured because of some of the proposed solutions to the solar neutrino problem. The more elegant and accepted solutions propose that neutrinos may oscillate from one flavour to another either in vacuum or in the presence of matter. A non-unity ratio of the CC and NC rates, corrected for the differences in cross-section, in SNO would be an excellent indicator of neutrino oscillations. As none of the proposed solar model solutions manage to explain the body of results from previous experiments, without drastic changes to the model, one must look towards other solutions such as oscillations. These solutions, if proved correct, will lead to physics beyond the existing standard model of Electroweak interactions that describe the behaviour of neutrinos.

An array of thousands of photomultiplier tubes serve to collect and detect the luminous Čerenkov signals that the electrons (born of the CC reaction) produce as they travel through the heavy water. The unique and important NC reaction is detected through the reactions of the photons emitted during the absorption of the neutrons on chlorine (added to the heavy water as ordinary salt) or by a set of dedicated discrete counters (tubular nickel ^3He filled proportional counters). As with all past detectors, the expected daily neutrino signal is quite small; SNO for example expects to see about 10 NC events per day. Despite the remarkable lack of interference from muons, there are other more insidious sources of background which cannot be overlooked or underestimated. Considering the tonnage of materials such as water, salt, acrylic, PMT glass, stainless steel, and cables to name but a few, even trace amounts of long lived radioactive elements can give rise to bothersome levels of background signals. Elements such as ^{238}U and ^{232}Th with astronomically long half-lives (on the order of 10 billion years) eventually produce harmful gamma rays energetic enough to mimic neutrino events for both the CC and NC channels. Absolutely everything contains some level of uranium or thorium, however minute the amount, and this must be controlled and known. For example, the heavy water must not contain more than 3×10^{-15} grams of ^{232}Th per gram of water in order to keep the background below 10% of the expected neutrino signal. Since the thorium level in heavy water is not already that low, it must be reduced. The problem remains as to the choice of all the detector components and what cannot be obtained clean must be made clean.

Obtaining, maintaining, and monitoring a low enough thorium and uranium content in the heavy water is the most critical aspect of the detector because of the fact that the heavy water is the heart of the detector. The obtention and maintenance of the low level of thorium is therefore the main task of the heavy water purification system. Of even greater importance is *knowing* as accurately as possible what the level of thorium actually is, a responsibility born by the monitoring techniques. Since day to day background determinations may be required,

the monitoring technique employed obviously cannot rely on direct detection of Th. Two daughters, radium and lead, are also removed from the water along with the thorium and they are both suitable for assay. Two different monitoring techniques have already been established which rely on radium, namely the Cryodetector and the Electrostatic chamber. Both systems rely on the extraction of radium onto column absorbers from which the emanated radon gas is whisked into a counting chamber. Both techniques are sensitive enough, but what of any possible disequilibrium in the thorium or uranium chains? Radon being a gas and thus mobile, can emanate from all detector components and decay to long lived lead in the heavy water. Since radium, and not radon, is extracted for the Cryodetector and the Electrostatic counters, any disequilibrium from external sources of radon are not sampled. SNO cannot afford to take its chances with the background levels; they must be determined as accurately as possible. It is therefore imperative that an alternative assay method be employed which does not rely on radium or radon. In order to monitor for the disequilibrium, a daughter after radon must be sought. The monitoring of lead is the only possible way. As the last long lived element after ^{220}Rn , ^{212}Pb ($t_{1/2} = 10.64$ hours) is the only available candidate that does not decay away completely while it is being concentrated. At about one atom per tonne of heavy water, the preconcentration of lead is a necessity and this is achieved with the use of the Reverse Osmosis (RO) portion of the purification system.

In this thesis, a technique for the assay of ^{212}Pb is presented which is based on three steps: Reverse Osmosis for preconcentration, elution for separation, and precipitation for source preparation. The RO can sample 288 tonnes of D_2O in 24 hours because it operates at 200 lpm, which represents essentially 288 atoms of lead since in the RO, the lead is in the presence of Th and is therefore still supported (unsupported sources notwithstanding). The term supported means that the parent radionuclide (Th in this case) is present with it's daughter (Pb) and therefore maintains the Pb activity. After preconcentration down to a mere 350 cc, a two part chemistry procedure lasting four to five hours separates the lead from

EDTA (a complexing agent added to the D_2O to help RO separation), and produces the thinnest possible precipitated source of $PbCrO_4$. A thin source is essential due to degradation of the alpha particle energies from self-absorption. By keeping the background levels to a minimum for all the steps involved before a countable source is made, the low signal from the high energy alpha of one of the ^{212}Pb daughters (^{212}Po at 64% branching ratio) can be detected with sufficient sensitivity to yield a calculable Th concentration for the sample.

The chapters and sections of this thesis are organised in a quasi chronological fashion similar to the structure of the brief introduction above. As a continuation of the introductory chapter, we begin with A Precip of The Standard Solar Model in section 2.1 of chapter 2. Sufficient details are given for a basic understanding of what is required for and involved in the calculation of the neutrino fluxes which are the object of several longstanding and recent experiments. A better appreciation and understanding of the solutions which pertain to the solar model will also be possible. Chapter 2, The Solar Neutrino Problem, continues with an overview of the pioneering experiment by Davis et al (section 2.8) entitled The First Solar Neutrino Experiment. Once the detector has been introduced, the first published results on neutrino astronomy are given in section 2.3 which is appropriately entitled The Birth of The Solar Neutrino Problem. After having given the impetus for further study in section 2.3, section 2.4 or Subsequent Solar Neutrino Experiments, goes on to introduce the experiments which were initiated several years after Homestake; namely Kamiokande I and II (section 2.4.1), SAGE (section 2.4.2), and GALLEX (section 2.4.3). A description of each experiment is given so that it is possible to understand the differences and failings of all the detectors. The observed neutrino flux are also given in comparison to the expected rate from the Standard Solar Model. The section on the Proposed Solar Neutrino Problem Solutions explores some of the many solar model and new physics oriented solutions (section 2.5) which have been proposed over the years. Some non-standard solar models (section 2.5.1) are discussed followed by neutrino vacuum oscillations (section 2.5.2),

matter oscillations (section 2.5.3), regeneration effects (section 2.5.4), the neutrino magnetic moment (section 2.5.5) and neutrino decay (section 2.5.6). Some of the implications of this new physics on Electroweak theory is also discussed (section 2.6). In section 2.7, the current results from all the experiments mentioned earlier are reviewed together and an attempt is made to interpret the results in terms of the effects that the postulated solutions manifest.

The apparent lack of success that most of the solutions have in explaining the results is one of the main reasons why so many scientists were eager to develop and build a new generation of detectors, namely Superkamiokande (section 2.8.1) and Borexino (section 2.8.2) which are presented in section 2.8 under the heading of Future Solar Neutrino Experiments. These detectors are contemporary to SNO and will be competitors when they finally come online. Another new generation detector, the Sudbury Neutrino Observatory, is the focus of chapter 3. The SNO project is important in the sense that it will provide one of the first flavour blind or total neutrino flux measurement along with a greatly improved electron neutrino energy spectrum, all with very good statistics. It is hoped that it will also provide answers as to which proposed solar neutrino problem solution is correct. In section 3.1, entitled What SNO Proposes to Measure and Why, details are provided for the three channels, as mentioned earlier, that are to be observed. The possible background modes associated with each reaction are also discussed. The detector design is then given, in section 3.2, with a focus on the all important cleanliness aspect of SNO. The importance of pure light and heavy water, beyond the fact that they serve as target material for neutrinos, is explored in section 3.3. Finally, in section 3.4 the two methods already mentioned of thorium assay via radium and radon are introduced and presented in sufficient detail. The proposed heavy water purification system, presented in detail in section 3.5, on which lead assay relies for the preconcentration of lead is discussed beforehand.

All considerations and work involved in the development of the necessary alternative lead assay monitoring technique is discussed in full detail in chapter 4.

The complete justification arguments for lead assay are then presented in section 4.1 followed by all the chemistry issues and expert opinions which served to guide the research in the right direction. All the details concerning the development of the chemistry procedures involved in making a countable α source are given in the order they were developed under section 4.4 for precipitation, section 4.5 for elution, and section 4.6 for reverse osmosis. Other issues are presented beforehand such as ^{212}Pb calibration sources (section 4.3) and the alpha counter employed (section 4.2). Once all the procedures have been established, a synopsis (section 4.7) of the results obtained with a discussion of the lead assay technique's capabilities, strengths, and weaknesses.

In chapter 5, the lead assay technique is first quantitatively compared with the Cryodetector and the Electrostatic detector which it was developed to complement in section 5.1. The last section (5.2) is the conclusion of the thesis wherein the final remarks are made as to the ultimate usefulness of the lead assay technique for the SNO detector. But, first things first, we begin as planned with some of the events and experiments which have shaped the field of solar modeling and neutrino astronomy.

Chapter 2

The Solar Neutrino Problem

2.1 Precipis of The Standard Solar Model

Throughout the history of humankind, many races and cultures have held a certain and often religious fascination for the Sun. Early twentieth century astronomers and physicists have also held a similar fascination for the Sun, although from the point of view of understanding it scientifically rather than veneration. The Sun has therefore been the object of observation and study from the early years to the modern era of science.

A variety of experiments were carried out in order to study the nature of the Sun and to try and force it to reveal its secrets about its formation, history, and the processes occurring within. Throughout the years, scientists carried out experiments and were able to measure the elemental constituents of the Sun and other stars by spectroscopic analysis. Among other parameters, they have also determined the surface temperature and luminosity, and observed the Sunspot activity that can only be seen on the Sun. As the data accumulated, theories were born and evolved with time which purported to explain the origins of the Sun (and all similar main-sequence stars) as well as explaining the energy generating processes within. The most successful theory to date, which addresses the above questions with the

exception of the origin of stars, has come to be known as the Standard Solar Model (SSM) [8]. Without yet delving into the finer details of the model, it can nevertheless be said that it is now generally accepted that the energy generating processes in the Sun are nuclear fusion reactions fueled by the few major constituent elements present in the deep interior.

Despite the seemingly imponderable nature of stars, scientists have managed to describe them in terms of a few simple nuclear reactions and equations of state. The framework for the energy generation part of the modern Standard Solar Model (SSM), which describes stars on a mathematical footing, was originally laid out by H. Bethe in 1939 [18]. At that time, the central temperature of the sun was believed to be hotter, thus, the dominant energy generating process was believed to be the Carbon-Nitrogen-Oxygen Cycle (CNO). Refined modern central temperature estimates have caused a shift towards the proton-proton (p-p) chain as the dominant energy generating process in the Sun [8]. In the interest of brevity, the description of the SSM will focus on Sol since it is the object of choice for study by terrestrial solar neutrino experiments. The parameters of importance which constitute the input to the SSM are discussed as follows.

Of primary importance are the low-energy cross-sections for the various processes which are believed to occur inside the sun. The cross-sections determine the reaction rates which are responsible for the radiation and thermal pressures as well as for the solar luminosity. The uncertainty in the cross-section factors is dominated by the uncertainties in the nuclear physics experiments and by the necessity to extrapolate the cross-sections down to the low energy regime of the stellar interior. The reaction rates at such low energies require prohibitively long time intervals before reasonable experimental results could be obtained, hence, direct measurements are not possible.

The p-p chain (figure 2.1) nuclear fusion reactions are the basis for 98.5% of the energy generated in the Sun's core [8], hence the term hydrogen burning. The carbon-nitrogen-oxygen (CNO) cycle, figure 2.2, originally proposed by Bethe produces the same amount of energy per cycle as the p-p chain, but it is now believed

to only make up the other 1.5% of the energy output. The CNO cycle is an elegant solution because the ^{12}C in the cycle acts as a catalyst and is therefore not generally consumed during the process of energy generation. The change in the theory from the CNO cycle to the p-p chain occurred as a result of the construction of accurate numerical models which predicted the current solar parameters only if the p-p chain was assumed responsible for the major part of the energy generation in the Sun. Had computers been available in 1939 or had the core temperature estimates been lower, Bethe might have come to the same conclusion originally.

Another input parameter which imposes strong constraints on the SSM is the solar luminosity (i.e., the solar constant) which is a well known quantity found to be $L_0 = (1372 \pm 4) \text{ W/m}^2$. It is defined as the total solar energy received normal to the Earth's surface (without the effects of the blanketing atmosphere) per second per unit area when the Earth-Sun separation is a mean orbital radius. The small uncertainty in the solar constant is what constitutes the strong constraint to the SSM or any would be solar model. No matter what is hypothesized to occur inside the sun, nothing must change the luminosity, and this simply because it is a well known experimentally determined constant.

The initial elemental abundances of hydrogen (X), helium (Y), and all other elements heavier than helium (Z) are needed in conjunction with the reaction cross-sections in defining the initial stellar reaction rates. When the fusion reactions in the sun are initially turned on, as it reaches the Main Sequence on the Hertzsprung-Russell diagram [24, page 47], the elements are assumed to be homogeneously distributed throughout. Data on the abundances of the elements from studies of the Earth, comets, and the visible solar surface are assumed to represent the initial elemental abundances of our immediate corner of the galaxy. Since the temperature of the sun's surface is below the threshold for fusion, it is believed that the preceding assumption on initial elemental abundances is valid for elements heavier than helium. A representative set of abundances, from Ross-Aller, can be found in Table IV of [10, page 776].

Figure 2.1: Diagrammatical representation of the p-p chain for the energy generation process in main-sequence stars.

Figure 2.2: Diagrammatical representation of the CNO cycle for the 1.5% energy generation in the Sun.

The radiation generated by the nuclear processes eventually makes its way out of the sun, but not without encountering the solar matter. The ratio of the total radiation produced, in a given spherical shell, to the flux leaving the surface of the shell is termed the radiative opacity. The opacity depends on the chemical composition of the shell and on complex atomic processes. The chemical composition plays a role in the following processes: photonic absorption by a bound orbital electron, photoionization, and Compton scattering. The sum of the effects of all these processes on the photon flux constitutes the opacity. The Rosseland mean opacity is what is generally used in SSM codes and must be calculated by Monte Carlo computer codes of which only a few in existence can simulate the prevalent complex stellar conditions. Inherently, the large uncertainty associated with the calculated opacity is carried over to the neutrino production rates.

The equation of state ($\frac{dP}{dr} = -\frac{m(r)G\rho}{r^2}$) from [8], which embodies the balance of the pressure gradient and the gravitational force of a shell of mass $m(r)$ a distance r from the center of the sun, is one other input parameter in the SSM. Since the sun obviously hasn't collapsed onto itself, the gravitational weight of the solar plasma must be balanced by the radiation pressure, on the plasma, from the photons, born of the nuclear reactions, and by the thermal agitation of the free particles and nuclei. The opacity of the ionized elements cause the photons to diffuse out in a randomwalk, hence the radiation pressure from the Compton scattering interactions. The sun is in a state of quasistatic instead of purely static equilibrium since very gradual changes occur during the long life span of the sun as a Main Sequence star.

The last, but not necessarily the least, of the input parameters is the solar age. Meteoritic ages are assumed to be very representative of the age of the sun where any discrepancy would be small compared to the time scale of interest. The accepted age of the sun is, therefore, $(4.6 \pm 0.1) \times 10^9$ years, as dictated by the age of meteorites [12, 66]. Meteoritic ages are determined by analysing the intrinsic ^{238}U ($t_{1/2} = 4.4683 \times 10^9$ years) and ^{232}Th ($t_{1/2} = 1.41 \times 10^{10}$ years) content along with the ^{208}Pb , ^{207}Pb , ^{206}Pb , and ^{204}Pb . From these relative quantities, researchers

can work out the age of the meteorite because of the long half-lives of U and Th.

In general terms, the sun produces energy over a very long time period because the center-of-mass energy of two interacting nuclei (of about 1.3 keV of energy each due to their thermal agitation) is well below the level of the coulomb barrier of the nuclei (about 0.7 MeV or more). At these very low energies, the reaction cross sections are also very small, hence the reaction rates are very low and must proceed via quantum mechanical tunneling. The mass difference is converted into energy, according to the Einstein energy mass relation, and as the fusion reactions take place, neutrinos and heat are produced. The neutrinos escape readily with virtually no interactions with matter, but the heat energy propagates slowly to the surface and is radiated from the Sun in the form of light. Like the photons, the neutrinos constitute a form of mass loss for the Sun through the energy they carry away, although it is essentially negligible in both cases.

All the input parameters introduced above are interdependent in one way or another. For example, the rates of the various reactions are determined by the low energy cross-sections, the elemental abundances, and the ambient temperature and density. Also, the opacity depends on the chemical composition as well and on reverse Bremsstrahlung. Changes in the nuclear reaction rates or the opacity will affect the pressure gradient in the sun (and hence the radius, temperature and density curves) as well as the luminosity, not to mention the neutrino fluxes. The only possible way to effectively model such a complex system such as the sun is numerically. The SSM is a set of encoded coupled linear differential equations which, when iterated for successive time steps, describe the sun from its birth to the present.

The output from the SSM constitute tables [12] of density, temperature, contribution to luminosity, neutrino flux, and elemental abundances versus radius, and of course the various neutrino spectra. Figure 2.3 below from [8, page 147] shows the SSM ν output as a function of the solar radius. The different ν detectors can therefore probe different regions of the Sun depending on which ν 's they are sensitive

Figure 2.3: Schematic of various solar ν flux versus solar radius.

to.

Figure 2.4 from [8, page 154] shows the most important SSM output, from a ν detector point of view, which are the ν fluences as a function of energy.

The uncertainties invariably associated with any predictions were calculated by running through the computer models with all input parameters fixed except for the one of interest. All parameters were treated similarly hence the effect of the variation of that given parameter on the output of the SSM could be evaluated. This was an important consideration from the neutrino flux viewpoint since the uncertainty in the neutrino flux must be evaluated in order to effectively compare measured fluences with predicted ones.

The problem remained to determine experimentally whether or not the proposed

Figure 2.4: Various solar ν flux versus ν energy.

p-p chain was what was really occurring at the stellar core as predicted by the SSM [8]. Up until the early 1960's, there had been no method by which the stellar interior could be probed, at least not until the Homestake experiment was carried out. None of the particles produced in the nuclear furnace, except for neutrinos, could yield direct information of the stellar interior. Photons emitted in the center of a star, for example, have a mean free path which is typically less than 10^{-10} [7] of the solar radius. The photons eventually make their way to the surface, after about one million years, but they no longer carry any useful information about the processes from which they were born. Neutrinos are the only particles which escape the stellar core virtually unaffected because they have such an extremely small cross section. The neutrino cross sections on the deuteron are typically about 10^{-42} cm² for 10 MeV neutrinos [28]. The cross section is defined as the transition rate of a given particle reaction per unit incident flux per target particle. Hence neutrinos, albeit once detected, would permit one to see the interior of stars.

Only one difficulty remained that had to be overcome and that was the method of detection of the neutrinos. The very property which permitted neutrinos to escape the Sun virtually immaculate would unfortunately also daunt experimentalists. How could a particle with such a low cross section be detected? The scientists of the Homestake experiment eventually overcame the difficulty in a rather elegant fashion. What was unforeseen was that this same experiment which set out to verify one of the SSM predictions also gave rise to a longstanding problem.

2.2 The First Solar Neutrino Experiment

Clearly, the intent of the Homestake group was to study the energy generating processes inside the Sun. They couldn't test for all the SSM reactions, hence, they concentrated their efforts on neutrino flux predictions for the ⁸B neutrinos [27, 26]. The experiment was based on the $^{37}\text{Cl}(\nu, e^-)^{37}\text{Ar}$ neutrino reaction for which the ⁸B neutrinos have the largest cross section (1.35×10^{-42} cm²) compared to the

other solar neutrino sources. Hence, the observations were also limited to electron neutrino's of energies greater than the reaction threshold of 0.814 MeV.

Only ^{37}Cl is needed for the experiment (with a natural abundance of 24.23%) which is found in the 520 tonnes of chlorine of which 126 tonnes is ^{37}Cl . 390,000 litres of liquid tetrachloroethylene (C_2Cl_4) which is contained in a horizontal cylindrical steel tank provides a cheap source of chlorine. C_2Cl_4 was ideal in the sense that it was readily available in large quantities since its original use was as a dry cleaning fluid. It also has a high Cl content, of which 24.23% is the desired ^{37}Cl , which was the target material for the detector. The tank was situated deep in the Homestake mine, at the depth of 1.59 km of rock or 4100 metres water equivalent (mwe), in order to minimize the cosmic-ray induced neutron background. The term metres water equivalent is used so that comparisons can be made of the muon attenuation that the different types of rock produce. The depth of water equals the depth of rock times the average specific density of the rock. Neutrinos interacting with chlorine produced ^{37}Ar which has a half-life of 35 days. A small amount of stable ^{36}Ar carrier was also added periodically to the C_2Cl_4 to ensure that the produced ^{37}Ar could be efficiently extracted. It would be very difficult to remove a few atoms of argon unless they were mixed in with sufficiently numerous stable argon atoms. After some time had elapsed, as the number of ^{37}Ar atoms increased, the argon would then be extracted and counted.

During several hours, helium gas would be bubbled through the C_2Cl_4 at a high flow rate to extract the argon carrier along with the ^{37}Ar . The extraction efficiency was typically 95% and varied somewhat from one extraction to the next. As the helium would exit the tank, it would pass through a condenser kept at -40°C and a molecular sieve both of which removed the C_2Cl_4 vapors. A 77 K charcoal trap extracted argon from the helium which would be returned to the tank. The argon would then be desorbed from the charcoal and transported by a small amount of helium to the next purification stage where the argon would be separated from the undesirable rare gases krypton and xenon. The presence of small amounts of

the rare gases was unavoidable because of contact with the atmosphere during the commissioning stages. After two stages of gas chromatographic separation, the level of krypton, for example, would be 1×10^{-8} parts by volume. The purified argon fraction would then be counted in a small proportional counter shielded against background radiation by a 30 cm thickness of iron. A ring of proportional counters straddling the main counter were used for cosmic-ray muon identification. Initially, the counters were not situated underground with the detector, but were eventually moved there to minimize the cosmic ray induced background in the counters.

The latest [40] background levels observed in the Homestake experiment were on the order of 0.055 ± 0.015 ^{37}Ar /day or 0.29 ± 0.08 SNU for cosmic ray induced events and 0.025 ± 0.025 ^{37}Ar /day or 0.13 ± 0.13 SNU from the average neutron background. The Solar Neutrino Unit, or SNU, has become the standard unit for solar neutrino experiments and represents 1×10^{-36} neutrino events per target atom per second. The unit of SNU itself is very suggestive of the necessary detector sizes and time periods necessary to carry out meaningful experiments in the solar neutrino field. Large numbers of target atoms are required in order to maximize the signal in a given time. The Homestake detector has a total of about 2.18×10^{30} atoms of ^{37}Cl and acquires data during a month before extracting and counting. In doing so, it is obvious that the data is an time integrated solar neutrino flux with no spectral or directional information.

2.3 The Birth of The Solar Neutrino Problem

The SSM predictions for Cl based experiments, as for all others as well, are calculated by adding up all the contributions from the different reactions in the p-p chain which yield neutrinos of energy above the detector threshold. Table 2.1 below [40, page 333] lists all the separate neutrino flux contributions from the p-p chain reactions for several different types of target nuclei.

Of interest for the moment are the capture rates for ^{37}Cl which represent a total

Target	p-p	pep	hep	^7Be	^8B	^{13}N	^{15}O	^{17}F	Total
^2H	0.0	0.0	0.02	0.0	6.0	0.0	0.0	0.0	6.0
^7Li	0.0	9.2	0.06	4.5	22.5	2.6	12.8	0.1	51.8
^{37}Cl	0.0	0.2	0.03	1.1	6.1	0.1	0.3	0.004	7.9
^{40}Ar	0.0	0.0	0.02	0.0	1.7	0.0	0.0	0.0	1.7
^{71}Ga	70.8	3.0	0.06	34.3	14.0	3.8	6.1	0.06	132.
^{81}Br	0.0	1.1	0.07	8.6	15.3	0.9	1.9	0.02	27.8
^{98}Mo	0.0	0.0	0.08	0.0	17.3	0.0	0.0	0.0	17.4
^{115}In	468.	8.1	0.05	116.	14.4	13.6	18.5	0.2	639

Table 2.1: Neutrino flux contributions from all p-p and some CNO chain reactions for 8 different target nuclei of interest.

of $7.9(1 \pm 0.33)$ SNU, where the uncertainty is three times one standard deviation (i.e., three sigma). The three sigma uncertainty means that any measured flux value lying outside the range defined by the uncertainty has less than one chance in 100 of agreeing with the predicted rate. The first published capture rate data for Homestake [27] was an upper limit of 0.3×10^{-35} ^{37}Cl captures per second, or 3 SNU. The most recently published Homestake data (Neutrino '94, to be published), for runs 18 to 124, quotes a capture rate of (2.55 ± 0.25) SNU at the one sigma level. The minimum SSM prediction of 5.3 SNU does not overlap with the maximum Homestake measurement of 3.3 SNU, this time at the three sigma level. The difference between experiment and theory exceeds the more than ample range of uncertainties, hence the solar neutrino problem (SNP). The data also suggested the existence of an anticorrelated neutrino flux and eleven year sunspot cycle. The SSM predicts a constant neutrino flux.

Ultimately, the SNP generated considerable interest both from theorists (see Chapter 3 below) and experimentalists. New detectors were subsequently built in order to verify the Homestake measurements or explore other solar neutrino fluences.

2.4 Subsequent Solar Neutrino Experiments

2.4.1 Kamiokande II & III

The Kamioka Nucleon Decay Experiment (Kamiokande), as the name suggests, was originally built to measure or set limits on the proton lifetime. It later became apparent that solar electron neutrinos could also be detected with the same detector arrangement plus a few modifications, hence Kamiokande II (KII) [33] was born.

Kamiokande is a water Čerenkov detector with a fiducial volume of 680 tonnes of purified light water, out of a total of 3000 tonnes, surrounded by 948 127 cm diameter photomultiplier tubes (PMTs) covering about 20% of the detector's surface. It is situated 1 km underground which provides 2700 mwe shielding from cosmic ray induced muons. KII employs light water as a neutrino target, hence only the neutrino on electron elastic scattering reaction can be detected. The low energy cutoff point, an effective minimum electron recoil energy of 7.5 MeV, is mainly governed by the background wall from the radioactive isotopes present in the water. An outer array of PMTs provided vetoing for muon signals and any other external sources, and most of the extra water tonnage served as shielding for external background sources as well. The water employed in KII was purified down to the level of less than 0.24 nCi per litre of uranium and radium.

The purity levels were achieved with a multistage water purification system consisting of five membrane filters at various points in the loop, a chelating agent ion exchanger for uranium removal, and mixed bed ion exchangers for removal of divalent metals. The divalent metals, namely Fe^{++} , Ni^{++} , Co^{++} , to name a few, as well as bacteria and other organics, were responsible for an unacceptable level of light absorption hence the necessity for their removal. The attenuation length of light after purification was ultimately greater than or equal to 35 m. Such a long attenuation length implies that only a small number of the Čerenkov photons would be absorbed thus maintaining a high signal intensity.

Kamiokande II acquired data for 1040 days from January 1987 to April 1990 with an upgrade near midstream, and obtained a ^8B electron neutrino flux $0.46 \pm 0.05(\text{stat}) \pm 0.06(\text{sys})$ times the predicted SSM flux of 6.1 SNU [12]. The midstream electronics upgrade permitted the lowering of the recoil electron energy threshold from 9.3 MeV to 7.5 MeV. No statistically significant signal difference resulted. Despite the low flux detected, the existence of ^8B neutrinos of solar origin was demonstrated with the correct energy and distribution above 7.5 MeV. Fortunately, the data showed no variation with time in the neutrino flux, as predicted by the SSM, but which is in apparent contradiction to the Homestake result. It is clear that much better statistics are required before the question of the variability of the flux can be resolved.

Between the months of April and December of 1990, Kamiokande effected some repairs and upgrades to the detector and electronics. During those few months, collaborators replaced burned-out PMTs, replaced the electronics with a new low power consumption high density system, and retrofitted the PMTs with conical reflective light collectors made of aluminized plastic, hence Kamiokande III [50]. Despite the massive changes and improvements, the results from KIII agreed with those of previous runs and did not show any sign of variance with sunspot activity above what was already established.

2.4.2 SAGE

An alternate radiochemical experiment, which began acquiring data in 1988, was born of a Soviet-American collaboration. The Soviet American Gallium Experiment (SAGE) [1] employs the $^{71}\text{Ga}(\nu, e^-)^{71}\text{Ge}$ reaction instead of the similar ^{37}Cl reaction of Homestake. The major advantage of SAGE over Homestake resides in its ability to detect low energy p-p electron neutrinos (0 to 0.420 MeV) above the 0.233 MeV threshold (Q value for the above Ga to Ge reaction.) Obviously, SAGE can also detect neutrinos from all p-p sub-chains as well as from the CNO cycle.

SAGE is situated in a cavity below a 4715 mwe rock overburden in the Northern Caucasus Mountains (Mount Andyrchi) at the Baksan Neutrino Observatory in Russia. The fiducial volume of gallium was originally 30 tonnes which was later increased to 57 tonnes in the summer of 1991. Of the 30 or 57 tonnes of gallium, ^{71}Ga represents only 12 and 22.7 tonnes respectively due to its 39.9% natural abundance. The laboratory walls were also covered with 60 cm of low-radioactivity concrete in order to reduce the neutron and gamma background originating from the surrounding rock.

The extraction procedure being as simple as it was for Homestake, except for the obvious difference in the chemistry, was worked out by Bahcall beforehand in 1978. The process hinges on the low melting point of gallium of 29.8°C allowing for the gallium to be kept in a liquid state, thus facilitating extraction by chemical means. The total mass of gallium was contained in eight 2 m^3 Teflon lined containers called reactors each containing less than 7 tonnes. Initially, a total of $700\text{ }\mu\text{g}$ of natural Ge carrier (as a Ga-Ge alloy) would be separated into equal amounts and thoroughly dispersed mechanically among the eight reactors, after which the reactors were allowed to sit undisturbed for a typical four week exposure time to solar neutrinos. The subsequent extraction was done by adding a solution of purified HCl (1 kg at -15°C) and H_2O_2 (5.2 kg) in 68.8 kg of water at $+4^\circ\text{C}$. The cooling of reagents was necessary to limit the heating from this exothermic reaction as the peak temperature of the Ga reaches 50°C . The reactor contents would be vigorously stirred during the course of the reaction which lasts for 25 minutes before the H_2O_2 would be completely consumed. The emulsified Ga containing fine globules, to which the dissolved carrier and neutrino-genic Ge has migrated, would then be recuperated by stirring with 37 l of 7N HCl for about one minute before being siphoned away. A second, but weaker, wash with 20 l of 0.5N HCl would increase the total extraction efficiency to a maximum (typically 80%) without dissolving more than 0.1% of the Ga metal in total for both extractions, a requirement which effectively limited the extraction efficiency to the maximum above. A precautionary 100 l solution of 1N

HCl) would then be added after the wash to prevent Ga oxidation and would be discarded prior to any subsequent extraction following another four week exposure period.

The combined solution from all eight reactors would then be reduced in volume by vacuum evaporation followed by several other steps involving purified reagents. The final stage would be the synthesis of germane (GeH_4) from the purified sample of Ge. The germane gas (20%) would then be added to a known quantity of Xe (80%) to improve the gas counting characteristics before being placed inside a proportional counter (PC). The Ge would decay to Ga, with a half-life of 11.43 days, by orbital electron capture from the K (88%), L (10.3%), or M (1.7%) shell giving rise to low energy Auger electrons and X-rays as the electron shells relaxed. Only the Auger electrons and the X-rays were detected in the PC. The PC, with the above gas mixture at 600 mTorr, would typically give 18% energy resolution at 5.9 keV with a K peak detection efficiency of 37% for the 10.4 keV Auger electron and a L peak efficiency of 34% for its 1.2 keV Auger electron. The PC itself was placed inside a NaI detector which was shielded by 2 cm of high purity copper and 20 cm or 30 cm of high purity lead or steel respectively.

The background contribution, from all sources internal or external, was found to be a total of no more than 1.3 SNU which represents no more than 1.0% of the predicted SSM signal in ^{71}Ga . The fourteen data runs from 1990 to 1992 yield a best fit result of $(73 \pm 18 - 16(\text{stat}) + 5 - 7(\text{sys}))$ SNU. The SSM predictions were of $(132 \pm 21 - 17)$ SNU by Bahcall-Pinsonneault (B-P) [11] and (122.5 ± 7) SNU Turck-Chieze-Lopes (TC-L) [62]. Once again, the observed neutrino flux was well below the predicted flux.

2.4.3 Gallex

The second gallium experiment to date, GALLEX [3, 4], began taking data in 1991 and would corroborate the SAGE results, unless one of the two experiments

were hindered by an unaccounted for background process. Situated at the Gran Sasso Underground Laboratory in Central Italy, GALLEX has roughly a 3300 mwe rock overburden protecting it from cosmic ray induced muons. There are general similarities between SAGE and GALLEX because of the fact that they both use the same target nuclei. The same $^{71}\text{Ga}(\nu_e, e^-)^{71}\text{Ge}$ process occurs as with the detection mechanism of Electron Capture (EC) of ^{71}Ge , where the main difference lies in the germanium extraction procedure and concentration chemistry. Hence, GALLEX is sensitive to the same neutrino signals as SAGE with the same threshold energy of 233 keV and all the same SSM predictions.

The 30.3 tonnes of refined gallium, of which 12 tonnes are ^{71}Ga , exists as a 2 M aqueous solution in a 70 m³ PVDF lined vinylester resin body glass fiber reinforced tank. The materials, including the glass fibers, were chosen with low uranium and thorium content. The high chlorine concentration, from the added HCl, and hence, the acidity, ensure that the germanium is in the form of GeCl_4 which is well suited for gas flow extraction techniques. At the onset of a data run, about 1 mg of ^{72}Ge , ^{74}Ge , or ^{76}Ge carrier is bubbled into the Ga through a pipe 1 m below the surface over a period of 10 minutes. A gentle stirring effect is achieved by bubbling nitrogen, in a closed loop, for nine hours. The cyclical and sequential use of three different carrier isotopes permits the determination of the amount of carrier carried over from previous data runs. After the Ga has been exposed undisturbed for a little over three weeks to the solar neutrino flux, the carrier and ^{71}Ge generated by solar neutrino interactions would be extracted by the bubbling of 1900 m³ of nitrogen gas, obtained from boil off of liquid nitrogen, for a period of 20 hours at 20°C.

The GeCl_4 extracted by the nitrogen could then be concentrated down to a smaller volume (50 ml) in a few steps before being transformed into germane (30%) and mixed with xenon (70%) to form the PC gas.

The employed PCs, of 1 cc internal volume, were constructed from low radioactivity Suprasil quartz with a 13 micrometer diameter tungsten anode wire fused

into the quartz ends. The gas was kept at a slight overpressure in the chambers. The PCs would then be placed inside a tight form fitting copper and low-activity lead enclosure situated inside a lead shielded counting room containing a low radon atmosphere. As was the case for SAGE, GALLEX would detect the resultant Auger electrons and X-rays from the electron capture of ^{71}Ge , namely the 1.17 keV L-peak and the 10.37 keV K-peak. The combined detection efficiency for both peaks was $(66 \pm 4)\%$. Of the fourteen atoms expected to be generated in the gallium over a three week period, only four are to be seen in the PC during the average 21 day counting period. Once the germane sample has been counted, the germanium carrier isotope content is determined by Atomic Absorption Spectroscopy (AAS). The ratio of the measured isotope amount present in the PC to the known amount initially mixed into the gallium yields the extraction efficiency for the entire process, typically $(99.8 \pm 3.7)\%$.

The various background processes are seen to contribute to the overall neutrino signal via the dominant reaction, $^{71}\text{Ga}(p,n)^{71}\text{Ge}$, requiring protons which can be produced by various methods. The cosmic ray induced muons, which subsequently generate free protons, generate a (3.7 ± 1.1) SNU signal, and similarly, the actinides (mainly U, Th, and Ra) produce roughly a 0.2 SNU signal. Fast neutrons are responsible for (0.15 ± 0.10) SNU, ^{222}Rn tagging errors (2 ± 1) SNU, chemical yield (± 1.5) SNU, counting efficiency (± 3.6) SNU, and finally, rise time cuts (± 1.8) SNU. The observed solar neutrino signal, with all above effects folded in, was found to be $(78 \pm 13(\text{stat.}) \pm 5(\text{syst.}))$ SNU at the one sigma level. This falls short of the B-P SSM prediction of $(132+21-17)$ SNU as GALLEX detects only 60% of the expected flux. Nevertheless, the SAGE and GALLEX results agree at the one sigma level as they at least should. Again, no temporal variations were evident.

2.5 Some proposed Solutions to The Solar Neutrino Problem

The SNP prompted many astrophysicists and particle physicists to reconsider some of what was assumed and taken for granted in the SSM and the standard model of electroweak interactions (QED). Either the solar model was defective or lacking, or there was to be some new physics involved beyond the standard model (see Ref.7, Chapters 5 and 9.)

To begin with, and what might seem as the most obvious conclusion in light of the Homestake data, assuming that Davis et al. did not overlook something in their analysis, was to lay blame to the SSMs solar core temperature prediction. Since the ${}^8\text{B}$ neutrino flux was very sensitive to the core temperature (the flux is proportional to the eighteenth power of the temperature), an effective lowering of the said temperature would also reduce the neutrino flux. A few non-standard solar models were proposed in an attempt to accommodate a lower core temperature in the SSM, such that the predicted and measured neutrino fluences agreed. Other attempts included a rapidly rotating core and strong magnetic fields, to name a few. Most of the non-standard models also exploited the weaknesses of the SSM, i.e., those aspects of the model where assumptions were made.

2.5.1 Non-Standard Solar Models

One of the most plausible of the proposed new models was the low Z core model. The opacity in the core depends on the heavy element content above helium, among other things. By reducing the fraction Z/X of heavy elements to hydrogen by a factor of 10, the opacity effectively no longer appreciably depended on Z , but rather only on electron scattering and inverse bremsstrahlung on hydrogen and helium nuclei, and hence was lowered. As the temperature gradient depends on the opacity, a lower opacity would then mean a lower core temperature. In course terms, a reduction

in the insulating efficiency results in a lower interior temperature. The net effect would be a ^8B neutrino flux reduction by a factor of seven with a new ^{37}Cl capture rate between 1.4 to 1.6 SNU, in agreement with both Homestake and Kamiokandell results. The difficulties arise when the acoustic p-wave spectrum is calculated and compared to the known spectrum. The small disagreement between the SSM and the measured p-wave frequency spectra worsens. A detailed discussion of p-waves and other similar waves is beyond the scope of this thesis, nevertheless, suffice it to say that these waves are pressure waves propagating in the Sun as sound waves would in the Earth's crust or mantle. The difference being that the solar waves are standing waves in the Sun's body which have rich and specific frequency spectra that have been accurately measured [71].

An iron precipitation model was also proposed and is very similar to the low Z model in that iron wouldn't contribute to the opacity if it had precipitated out of the gaseous form it was assumed to be in. Assumptions were of course made concerning the feasibility of such a precipitation, but from the point of the effect on the opacity, it was identical to the low Z model.

Another model, aptly coined 'a mixed up core', proposed some form of mixing between the core and outer regions of the sun in order to keep the hydrogen fraction constant thus preventing the depletion of hydrogen in the core. If the core were to be depleted of hydrogen, the temperature would rise due to an increase in opacity (from a greater abundance of higher Z matter) thus resulting in an increase in luminosity. A constant hydrogen fraction (the result of continuous mixing of the core and convective zone), on the other hand, would prevent the increase in core temperature and restrict the ^8B flux accordingly corresponding to the levels observed in modern times. Numerical simulations of the SSM with convective mixing required that the mixing have occurred from the initial firing up of the Sun to date and over at least 60% of its mass. Only under such drastic conditions could the results agree with the Homestake data.

A strong magnetic field in the solar core was also postulated. The equation

of state would include a new term for the magnetic pressure which increases the pressure gradient for a field decreasing in the direction of the surface. Numerical calculations were carried out and it was concluded that a field on the order of 10^9 Gauss was required for there to be any significant changes to the neutrino flux. Unfortunately, the model behaved contrary to its intent, indeed, as the net result was to double the predicted ^{37}Cl rate for Homestake instead of reducing it.

Most of the proposed non-standard solar model solutions, including those mentioned above, suffer from the lack of rigorous testing since detailed models were never constructed and evaluated as the SSM was (à la 1000 standard solar models of Bahcall.) Some of them even rely on more unproven assumptions. The net result, after a few decades, has been that the general expectation has gravitated towards a new physics related solution rather than a non-standard solar model solution, despite the fact that none of the solar model solutions have been ruled out decisively. The previous discussion on non-standard solar models has not provided a really compelling solution to the SNP, whereas the arena of new physics beyond the standard model of electroweak interactions has. If the solar astrophysics were not to be at fault, then something must be happening to the neutrinos enroute to Earth.

2.5.2 Vacuum Neutrino Flavour Oscillations

What can happen to an electron neutrino, for example, such that its detection rate at Earth is reduced enough to agree with Homestake and KamiokandeII results? The vacuum of space offers far too little matter for there to be any appreciable probability for neutrino absorption, and the same goes for the low density (for the most part) of solar matter. The only alternative would be that a fraction of the electron neutrinos are somehow modified such that terrestrial detectors cannot 'see them'. Pontecorvo [53] was one of the first to suggest that the electron neutrino could be transmuted to a muon neutrino in the vacuum of space, which would

effectively reduce the electron neutrino rate detected because neither Homestake nor Kamiokande could detect neutrinos of any other flavour.

The mechanism by which neutrinos could oscillate requires that the observed neutrinos, which are electron, muon, or tau flavour eigenstates, be linear combinations of mass eigenstates ν_1, ν_2, ν_3 . It is not necessary, though, to discuss the effect between three states for the major features of interest to appear, hence only mixing between two states will be considered. Kayser [36] has pointed out that due to the Heisenberg Uncertainty Principle which implies that the spread of the momentum of the neutrino wave function must be greater than $\hbar/L_\nu$ (where L_ν is the vacuum oscillation length with the dimensions of metres), the treatment of neutrino oscillations should in reality be done with wave packets instead of the constant momentum approach below. The result of the wave packet method, however, is nearly always the same for most practical purposes, thus the constant momentum approach remains valid. For the specific case of ν_e 's oscillating to, for example, ν_μ 's, the square of the overlap of the time dependent flavour states, expressed as stated above as a linear combination of ν_1 and ν_2 , yields the probability of the ν_e becoming a ν_μ . The momentum of ν_1 and ν_2 are assumed to be equal, hence their energies (E_1, E_2) will be slightly different because of their masses m_1 and m_2 . The total probability for the sum of the ν_e remaining a ν_e and the ν_e becoming a ν_μ is constant at unity, hence the probability of the ν_e remaining as such can be expressed as [8]

$$|\langle \nu_e | \nu_e \rangle(t)|^2 = 1 - ((\sin(2\theta_\nu))^2)(\sin(\pi R/L_\nu))^2 \quad (2.1)$$

L_ν , the oscillation length, is $4\pi E/\Delta m^2$, and R is the distance travelled by the neutrino. If L_ν is expressed as $2.48(E/\text{MeV})(\text{eV}^2/\Delta m^2)$ metres, then the minimum solar neutrino mass squared difference that can be investigated at the Earth is $\Delta m^2 \approx 1.6 \times 10^{-12} \text{ eV}^2 (E/\text{MeV})$, where $\pi R/L_\nu$ was taken as 0.3.

The predicted event rate for solar neutrino sources, subject to vacuum oscillations between neutrino flavours, depends on the spread of the region of emission

in the Sun, the change in position of the detector where they are absorbed on the Earth (due to the eccentricity of Earth's orbit), and the energy spectrum of the emitted neutrinos. The first two parameters are both tied to variations in the distance travelled by neutrinos before detection and the third is tied to the functional dependence of the probability on the neutrino energy. The average over energy for typical solar neutrinos smooths out the effect from the distance variation and results in an average probability of

$$|\langle \nu_e | \nu_e \rangle(t)|^2 = 1 - 0.5(\sin(2\theta_\nu))^2 \quad (2.2)$$

In order to achieve low enough detection rates comparable to those already published by Homestake and Kamiokandell, the parameters in vacuum oscillations must be 'fine tuned' and be associated with a large mixing angle, θ_ν . It is for those reasons that neutrino vacuum oscillations are not favoured. The $\sin^2 \theta_c$ of the Cabibbo mixing angle in the quark sector is small (about 0.048), thus it is expected that θ_ν be small as well. The 'just so' oscillations neutrino mass squared value of about $5 \times 10^{-11} \text{ eV}^2$ is required for agreement with observation. With the above considerations, the parameter space $(\sin^2(2\theta_\nu), \Delta m^2)$ for neutrino vacuum oscillations is very limited indeed.

2.5.3 Matter Induced Neutrino Oscillations

Wolfenstein [67] in 1978 proposed an alternative method whereby electron neutrinos could oscillate to muon or tau neutrinos while passing through matter. Mikheyev and Smirnov [46, 45, 47] also contributed to the study of the effect, hence the name MSW (Mikheyev-Smirnov-Wolfenstein) effect.

Although neutrinos in the MSW effect still undergo vacuum oscillations, an extra term in one of the diagonal elements of the mass mixing matrix takes into consideration a specific charged current process. This process is the charged current ν_e - e^- scattering, which occurs only for the ν_e . Any neutral current terms which

represent ν_τ scattering on electrons and nucleons are neglected since they do not add to the MSW effect. The extra term in question is simply $\sqrt{2} \times G_F \times n_e$, which is essentially the product of the Fermi Coupling constant G_F and the electron number density, n_e . In essence, the extra charged current term causes the MSW's large mixing effect, as opposed to the much lower vacuum oscillations only mixing effect. Oscillations occur when the small energy difference between neutrino flavours is compensated for by the interaction of the ν_e with electrons, which is known as the resonance condition.

The presence of matter is implied, i.e. the Sun, since an ample supply of electrons is required. The survival probability of an ν_e must be calculated with due consideration for the existing density distribution in the Sun which has a very low density near the surface and is densest at the center ($\rho = 148 \text{ g/cm}^3$). As the ν_e , produced in the solar center, travels through the Sun, it traverses it in the high to low density sense. The initial ν_e flavour state, created in the central region, is essentially made up of the heavier ν_2 mass eigenstate under solar core conditions. The mass of the ν_2 decreases, following the electron density, as it travels through the Sun towards the vacuum of space. If the change in mass occurs slowly enough, there will be no transitions between the ν_1 and ν_2 states, hence, the ν_e remains essentially a ν_2 state. Since at low densities, the ν_2 mass state is associated with ν_μ (and the ν_e associated with ν_1), the ν_e emerges from the Sun as a ν_μ , and is effectively unseen by experiments sensitive only to the ν_e flavour state. For the rate of change in ν_2 mass to be small, the rate of decrease of the density must also be small, otherwise transitions between mass eigenstates will destroy the effect. The slow rate of change of the electron density has come to be known as the 'adiabatic condition'.

Ultimately, the expression for matter driven neutrino oscillations is very similar to that from vacuum oscillations alone (equation 2.1 above.)

$$|\langle \nu_e | \nu_e(t) \rangle|^2 = 0.5 + (0.5 - P_j) \cos(2\theta_m) \cos(2\theta_v) \quad (2.3)$$

The probability that a given mass eigenstate abruptly and non-adiabatically changes state, thus preventing some flavour oscillations, is

$$P_j = \exp -\pi \Delta m^2 \sin^2(2\theta_v) n_e / (4E \cos(2\theta_v) | n_e/dr |_{res}) \quad (2.4)$$

where $n_e > n_{res}$ and θ_m is the matter mixing angle from

$$\sin(2\theta_m) = \sin(2\theta_v) / D_m \quad (2.5)$$

and D_m is defined as

$$D_m = \sqrt{1 - 2(L_v/L_e) \cos(2\theta_v) + (L_v/L_e)^2} \quad (2.6)$$

At resonance, θ_m is $\pi/4$ because D_m equals $\sin(2\theta_v)$ due to L_v/L_e being equal to $\cos(2\theta_v)$. It is assumed that $m_2 > m_1$ in Δm^2 , otherwise the resonance condition wouldn't be satisfied and oscillations would not occur.

Not all neutrinos are born at the solar center, actually, each reaction occurs within a given range of the solar radius, and the range in question is obtained as part of the numerical solution of the SSM. In essence, a given neutrino flux is modulated by neutrino oscillations and must also be averaged over the region of production given in terms of the solar mass distribution.

A contour plot of Δm^2 versus $\sin^2(2\theta_v)/\cos(2\theta_v)$ can be made, given an experimentally determined neutrino flux, where isorate contours can be plotted for different experiments. The different experiments can therefore be compared in the parameter space of interest, namely the Δm^2 and θ_v space. As more experimental fluences becomes available for different solar neutrino sources, the isorate contours, which enclose allowed regions, map out the possible parameter space which is common to all experiments. The result of such an exercise would be the determination of the proper mass squared difference and vacuum mixing angle responsible for neutrino oscillations. The typical ranges of values in the parameter space wherein an

MSW solution of the SNP is expected to lie (also known as the solution space) are on the order of $10^{-03 \pm 1} \text{ eV}^2$ for Δm^2 with $\theta_\nu \geq 1^\circ$. The corresponding plots for the experiments who have reported results to date can be found below in subsection 2.7.

2.5.4 MSW Neutrino Flux Regeneration at Earth

The above theory is also as valid for the matter of the Earth as it is for solar matter, hence the Earth should also have some effect on the neutrino flux, which may or may not be measurable, given the proper electron number density conditions at Earth.

The geographical location of a detector can give rise to some temporal effects on the neutrino flux because the rotation of the Earth implies that there will be a variation in the path length in the Earth that the neutrino must travel [15, 16]. During the day, the path length is essentially the depth of the detector, but during the night the path is equivalent to the diameter of the Earth. It is expected that the net effect on the neutrino flux would be to increase it (assuming the solar matter decreased it in the first place.) If ν_μ 's, for example, were to travel into the Sun, they would undergo the reverse of the process described above. In essence, the Earth would regenerate the flux to some extent. The extent of the regeneration effect would only partially restore the flux since the path length in the Earth is much shorter than the Sun's, and the available density distribution between core and surface is also much less. Typically, the core density of the Earth varies from about 3 g/cm^3 ($n_e = 1.6Na$) on the surface to a maximum of 13 g/cm^3 ($n_e = 6Na$) at the core. The 'day-night' effect, as it is called, would have its greatest effect with the following $E/\Delta m^2$ ratio:

$$E/\Delta m^2 = 10^5 \cos(2\theta_\nu) [66 \text{ cm}^{-3} / (n_e / Na)] \quad (2.7)$$

As usual, E is in MeV, Δm^2 is in eV^2 , and n_e is in the range indicated above.

If 10 MeV neutrino's are considered, then Δm^2 would be about at the 10^{-06} eV^2 order with $\sin^2(2\theta_\nu) \geq 0.01$. It is apparent from the above expected parameters that regeneration in the Earth presents no new parameters in the study of solar neutrino's and their oscillations. The MS parameter space remains essentially unchanged as well, with some changes in rate affecting the form of the isorate contours only.

Besides the possible day-night effect from the Earth's rotation, there is the possibility of an effect due to the Earth's elliptical orbit which acts in combination with the day-night effect. The possible path length variations can be summed up as follows. Since the Earth is at aphelion during the summer months and the pole is inclined toward the Sun, the paths the neutrinos travel are shortest during the night compared to the other seasons for a detector in the northern hemisphere. The physical situation can be approximated by a two dimensional circular Earth lying on the same plane as a similarly defined Sun, hence, the path of the neutrinos are actually chords. In winter, at perihelion with the pole leaning away from the sun, the chord lengths are longest. Spring and fall chords are the same and lie in between summer and winter in comparison lengthwise. Thus, there would be low frequency seasonal fluctuations affecting mainly the average neutrino signal modulated by high frequency day-night oscillations. Provided the sensitivity is high enough, day-night effects should be observable in live detectors, not to mention the seasonal effect. Detectors which time-average the flux should only see the seasonal effect, given an adequate signal rate.

2.5.5 Neutrino Magnetic Moments

Neutrino's, it is speculated, may also have in addition to a small mass a small magnetic moment which implies they would be subject to spin flips, and hence helicity changes, in the presence of sufficiently large magnetic fields. The magnetic field component, transverse to the neutrino flight path, would be supplied by the Sun or the Earth. The resultant spin flip would change a lefthanded neutrino

into a righthanded one effectively rendering it undetectable since only lefthanded neutrinos interact with matter according to electroweak theory. The latter applies if the neutrinos are Dirac neutrinos and is referred to as flavour changing neutrino spin rotations. The required strength of the neutrino magnetic moment as reported by Bahcall [8] and by Akhmedov [2] is on the order of 10^{-10} Bohr magnetons with a transverse magnetic field of about $10^{-03} - 10^{-04}$ G. Under these conditions, the spin flip would occur in the convective zone of the Sun where the magnetic field fluctuates, increasing with the sunspot cycle every 11 years. The emergent neutrino flux would therefore be anti-correlated with the sunspot cycle.

If Majorana neutrinos were assumed, on the other hand, then the spin flip would result in the transformation of an ν_e into an $\bar{\nu}_e$ (a flavour conserving neutrino spin rotation.) The $\bar{\nu}_e$ would be detectable via the same reactions available to anti-neutrinos from supernovae. The necessary Δm^2 and transverse magnetic field conditions are the same as the Dirac neutrino case.

There exists a special parameter space wherein the neutrino spin flip effects could be separated from the MSW effects. The range of Δm^2 would need to be between 10^{-08} to 10^{-07} eV² with M (the ratio of the off-diagonal transition moment to the neutrino magnetic moment times the transverse magnetic field strength at the solar core) between 10^3 to 10^4 G. Within the range of those parameters, it is expected [2] that most of the ^7Be and ^8B neutrinos would be affected within the convective zone by the time varying (with the 11 year sunspot cycle) transverse solar magnetic field. For the flavour changing case, the ^{37}Cl data would be variable in time and anti-correlated with the sunspot cycle. Such a time variation would not be evident in the ^{71}Ga experiment. In both experiments, there would also be evidence of regeneration of the neutrino flux from the Earth provided Δm^2 was between $1 - 5 \times 10^{-06}$ eV² with $\sin^2(2\theta_\nu)$ at least 0.1. In contrast, the flavour conserving interaction wouldn't give rise to a regeneration effect and both ^{37}Cl and ^{71}Ga data would be anti-correlated with the sunspot activity cycle.

Unfortunately, knowledge of the solar magnetic field is poor which casts doubts

about any calculations concerning neutrino spin flips. Hence, the magnetic field strength is essentially a third parameter effectively preventing an unambiguous separation between MSW and spin flip effects.

2.5.6 Neutrino Decay

Most particles possessing mass decay with time albeit on different time scales. Why would the neutrino, assuming it has mass, be any different? The possibility of decay of a neutrino with finite mass may also be a solution to the SNP in that the neutrinos could decay in transit, given appropriate conditions of course. It is not expected [8] that neutrino decay will occur without the MSW effect occurring as well. Such is the case because of the observation of the electron anti-neutrino signal from the SN1987A supernova implying their stability for distances of at least 10^{10} AU, unless they oscillate via an MSW type effect. The general decay scheme proposed for the decay plus MSW mechanism consists of the initial ν_e oscillating via MSW to the ν_2 mass state and subsequently decaying to a $\bar{\nu}_1$ accompanied by a scalar (or pseudoscalar) boson. The $\bar{\nu}_1$ mass state would be a $\bar{\nu}_e$.

The effect on observations of neutrino decay coupled with MSW oscillations could best be visible in detectors sensitive to neutral current reactions. The energy that is available to the anti-neutrino after the parent neutrino has decayed is less because of sharing with another particle (the boson), a result which may render its detection difficult once detector thresholds are considered. Since the SSM predicts only neutrino's, the detection of 'solar' anti-neutrinos would be a good indication of neutrino decay coupled with the MSW effect.

2.6 SM Implications of ν Oscillations

Two of the above processes, vacuum and matter neutrino oscillations, require individual flavour lepton number non-conservation and, as stated earlier, imply that

	Leptons		Quarks	
	Q/e			
Gen	-1	0	+2/3	-1/3
1	e^-	ν_e	u	d
2	μ	ν_μ	c	s
3	τ	ν_τ	t	b

Table 2.2: The main fundamental constituents of the SM organized by generation. Antiparticles (not shown) have opposite charge and lepton numbers.

neutrinos have a non-zero finite mass. This constitutes physics beyond the Standard Model of Electroweak Interactions. In Electroweak theory (or Quantum Electrodynamics (QED)), the conservation of the individual e^- , μ , and τ lepton numbers is assumed since there hasn't been any theoretical basis from which it could be derived, and because analysis of the allowed (i.e. detected) reactions strongly indicate a conserved quantity. On the other hand, since Parity (P), Charge conjugation (C), and the combined PC are not valid conservation rules for weak interactions, there are no arguments which would tend to uphold the individual flavour lepton number conservation, apart from the lack of evidence against it. In fact, in many extensions of the SM, flavour lepton number conservation is not a feature, hence the observation of neutrino oscillations would be an indication of physics beyond the SM. Roughly the same argument applies to the neutrino mass issue. The SM does not provide a basis for the hierarchy of the masses for its constituent set of fundamental particles. The mass symmetry of the quark sector is not carried over to the lepton sector (table 2.2). Why would the neutrinos, the lower members of the lepton families, not have mass as the lower members of the quark families do? The answers to these questions are not provided by QED, one has to look beyond for a more fundamental theory of which the SM would only be a 'low energy' special case.

Of concern to cosmologists, is the issue of dark matter. Dark matter being

matter which doesn't emit photonic radiation, hence rendering it difficult to detect, is believed to be strewn throughout the universe. The visible mass of the universe has been shown to be insufficient to stop, by gravitational braking, the expansion of the universe. A sufficiently massive universe would eventually stop expanding and collapse in a 'Big Crunch', the opposite of the Big Bang which is theorized gave birth to the universe. The interest lies in determining the contribution of the missing mass to the total mass of the universe. The result would lead to a decision on which theory will most likely represent the ultimate fate of the universe: the ever expanding universe (due to an insufficient mass for closure), or the Big Crunch. The proposition that neutrinos could be massive, relatively speaking of course, sparked some new interest. Unfortunately, according to Bahcall [8], massive solar neutrinos cannot solve the problem of the ultimate fate of the universe.

What remains to be done are the experiments which will permit the resolution of the SNP and hopefully determine which of the myriad of proposed solution mechanisms best describe the data. The implications of the currently available data is therefore discussed in the following section.

2.7 SSM Versus Physics Based SNP Solutions and Experimental Results

In light of the theories put forth designed to explain the SNP and with the solar neutrino data presently available, the status of the various SNP solutions can be examined. So far, data has been reported from two different classes of experiments, namely Homestake, SAGE, and GALLEX (radio-chemical experiments), and Kamiokande a light water Čerenkov experiment. The radio-chemical experiments could only look at the time averaged neutrino signal (over three to four week periods) as opposed to the real time event by event detection of neutrinos as in Kamiokande. As shown in table 2.3, all detectors show a lower than expected solar

Detector type	Observed Rate SNU	Expected Rate SNU	Sources of Expected Rate (SNU)
KIII (H ₂ O)	2.7 $\pm 0.3 \pm 0.3$	5.8	All ⁸ B above 7.5 MeV
Homestake (³⁷ Cl)	2.55 $\pm 0.17 \pm 0.18$	7.9 ± 2.5	pp 0.00 pep 0.23 ⁷ Be 1.12 ⁸ B 6.15 ¹³ N 0.102 ¹⁵ O 0.34 ¹⁷ F 0.0034
SAGE (⁷¹ Ga)	73 +18-16+5-7	131.5 +20-16	pp 70.8 pep 3.01 ⁷ Be 34.4 ⁸ B 14.1 ¹³ N 3.77 ¹⁵ O 6.03 ¹⁷ F 0.06
GALLEX (⁷¹ Ga)	79 $\pm 10 \pm 6$	same as above	same as above

Table 2.3: Current solar- ν detector results: measured rates, neutrino type, expected rate, and different contribution sources for the expected rate. The second pairs of quoted uncertainties are systematic uncertainties.

neutrino signal.

Since the work by Bahcall and Ulrich (BU) [12], there have been several more published revisions of the SSM calculations and predictions. Contemporary to the BU SSM were the Turck-Chieze, Cahen, and Cassé (TCCC) [61] calculations. In 1992, Bahcall and Pinsonneault (BP) [11] presented a revised SSM which included helium diffusion, and in 1993 Turck-Chieze and Lopes (TCL) [62] published the latest revision which employed the best nuclear physics results to date to determine their effect on the predicted neutrino fluxes and helioseismology. All in all, some eleven different SSM calculations have been carried out in recent years [9]. The net effect of all these improvements, on average, were to modify the predicted solar

neutrino rates by about 10% or so. It should be clear, in light of all the small variations, that in order to sufficiently reduce the predicted solar neutrino fluences, drastic changes must be made to the SSM. Any attempts to drastically change the SSM would ultimately be confronted with those solar parameters which cannot be twiddled with, the most important and unwieldy being the solar luminosity and the helioseismological surface oscillations. In essence, the answer may lie with some new physics.

How can the low observed signals evident in Table 2.3 be interpreted? The uncertainties with SSM calculations, being what they are, cannot allow for all the low signals. If the minimal solar model is assumed (which supports only p-p neutrinos) to explain the gallium rates, then the Homestake and Kamiokande results must be wrong since they have detected non-negligible ^8B signals (non-existent in the minimal model.) It is difficult to believe, although definitely not impossible, that both Homestake and Kamiokande are wrong. According to Bahcall (Neutrino 94), based on the simple analysis of the Davis and Kamiokande results, if both experiments are correct, then new physics is in order, as opposed to a modified SSM. The one σ agreement between the SAGE and GALLEX results, despite the above, is important despite the differences in the chemical form of the target material. Any disagreement would have been an indication of a hitherto unaccounted for systematic error.

Other than the time averaged rate, the Homestake detector, because of its long running time, could also have observed an anti-correlation with the 11 year sunspot cycle. Unfortunately, whether such a conclusion can be made from the data is controversial [12]. More thorough analyses have not shown a significant level of anti-correlation. Kamiokande data also shows no apparent temporal correlation of any kind with sunspot activity. The average flux values calculated from the individual runs for Kamiokande II and III agree to one σ over the period of 1987 to near the middle of 1991. During that same time period, the sunspot activity (number) increased from a minimum near zero to a maximum of about 150 [50]. In addition,

neither SAGE nor GALLEX have observed any temporal neutrino fluctuations. The published data for SAGE to date covers the period from January 1990 to May 1992. GALLEX has published data, to date, on runs acquired during the time period of May 1991 to September 1993. So far, the fluctuations between individual runs have been consistent with statistical fluctuations and have not followed a decreasing trend that would be expected from a sunspot anti-correlation effect. Had the anti-correlation been established, on the other hand, it would have been a good indication of the existence of a neutrino magnetic moment. During periods of high sunspot activity, the solar magnetic field is strengthened, hence a number of the neutrinos could undergo a spin flip which renders them undetectable. Clearly, more data is required with better statistics and long running times.

The Kamiokande results, on the other hand, have shown, for the first time, that the detected neutrino signal is indeed coming from the Sun and the ^8B spectrum is as expected by the SSM. Had the MSW effect been the cause of the deficient neutrino rates, a characteristic modification of the neutrino energy spectrum would have been observed. The variability of the effect with neutrino energy may explain, in part, why no deviations from the expected spectrum were observed by Kamiokande. The threshold energy for Kamiokande being 7.5 MeV implies that the detector was not sensitive to most of the ^8B spectrum. The latter point combined with insufficient statistics may explain why a non-standard spectrum was not observed. Also, by the fact that ^8B neutrinos are themselves detected and confirmed, the dominant energy generation process in the Sun via the p-p chain has been established [33].

The MSW effect may yet be shown to be the cause of the SNP. Low neutrino fluences can still be obtained for certain ranges for the Δm^2 and $\sin^2(2\theta_{\nu})$ parameters. If the neutrinos underwent oscillations from one type to another as they traveled through the Sun, then the number of ν_e 's would be reduced, as a function of energy. Since all presently operational detectors are sensitive to ν_e 's only, they would register fewer events and report lower fluences. Thus, the MSW effect can explain the current data with success, although a unique solution cannot as yet be reached

[9, 17]. The current allowed parameter space is shown in figure 2.5. Presently, there are essentially two regions of acceptability, any one of which cannot be eliminated without new data from other experiments.

Obviously, no definitive conclusion can be made as to the cause of the SNP, in light of the available data, except that, generally speaking, more data is required. The neutrino spectrum must be measured with better statistics in order to differentiate between neutrino oscillations and non-standard SSM based solutions, and better statistics acquired over the short (for day-night oscillations) and long term (for the Sunspot anti-correlations) of at least a few 11 year cycles, are needed to settle the time varying signal issue. The data from new detectors under construction is eagerly awaited in the hope that their data will differentiate between the possible SNP solutions.

2.8 Future Solar Neutrino Experiments

In order to detect neutrinos in greater numbers in response to the need for increased statistics, the new generation of detectors must either be scaled up versions of already existing ones or use target materials which have higher neutrino absorption cross sections. Needless to say, in both instances, the background levels must be carefully controlled. Two of the many possible detectors proposed to date are presented below: Superkamiokande, which is an example of a scaled up detector as the name suggests, and Borexino, which uses a target material different from all those employed so far.

2.8.1 Super-Kamiokande

The simplest way to increase the number of detected neutrino events for a Kamiokande type detector, since water was the target material, would be to build a new one of much larger proportions, hence the name Super-Kamiokande (SK). The collabora-

Figure 2.5: MS plot of Δm^2 vs. $\sin^2(2\theta_\nu)$ for all published detectors to date. The shaded areas are the parameter spaces wherein the ν oscillation solutions remain possible.

tors already had the experience and knowhow from the original Kamiokande detector, thus, it is expected that building a larger version would be no more difficult.

The 58 m high by 40 m diameter cavity where SK is being built is situated 1 km underground in the Gifu Prefecture (250 km west of Tokyo) [30, 5]. The same design, employed for the earlier Kamiokande detector, would also serve for SK except that the diameter of the detector (still in cylindrical form) would now be 40 m with a height of 41 m. The total volume of water would then be 50,000 m³, of which only an "effective" 32,000 m³ would constitute the fiducial volume for the outer PMTs array. The outer array, consisting of 2000 Hamamatsu 20 cm PMTs, will be separated from the inner one by 2 m of water and a black plastic lining stretched onto the inner counter PMT support structure. The photocathode coverage of the inner counter array would be on the order of 40% because of the 11,200 50 cm PMTs. A 22 ktonne fiducial volume will be available for the inner PMTs. The expected spatial, angular and energy resolution would be about 50 cm, 27°, and $14/\sqrt{E/10\text{MeV}}\%$, respectively for the inner array.

Because of the increased amount of water available as target material for solar neutrinos, the predicted event rate, according to the SSM, would be 67 events per day, although at 0.46 of the SSM flux, only a maximum of 31 events/day could be seen in actuality. The design energy threshold is 6.5 MeV which, it is expected, will be reduced over time to 5 MeV. At 5 MeV, the event rate will be roughly 20 per day, at which rate a years worth of data would amount to 7,300 ν 's: very good statistics indeed. All this, of course, hinges on the ability to control the background levels in the detector which, unfortunately, will remain high with respect to the signal as it was in KII. The observed ν 's for Super-kamiokande would be detected as before, via the Čerenkov photons emitted from elastic scattering off of electrons. The directionality of the recoil electrons will remain the signature by which the solar neutrinos will be separated from the background. The solar origin of the neutrino induced signals will also be demonstrated by the directionality of the recorded events.

The main contribution that SK will bring to the issue of the SNP will be a more accurate measurement of the ^8B neutrino energy spectrum. Any deviations from the expected spectrum would be direct proof of a non-astrophysical solution to the SNP. The construction of the detector has been on schedule so far, and it is expected that it will come online in early 1996.

2.8.2 Borexino

Very similar in design to the SNO detector (see Chapter 4), the Borexino detector [5] proposes to explicitly measure, for the first time, the ^7Be neutrinos (which will be 90% of the total expected signal.) The main reaction by which neutrinos will be seen involves the capture of elastically scattered electrons, of energy above 0.25 MeV, by a liquid scintillator. The experiment will be setup at the Gran Sasso Underground Laboratory in Italy where the rock overburden affords a 3300 mwe of muon shielding (same as GALLEX.)

The basic design of Borexino begins with a central spherical volume of 300 tonnes of high radio-purity liquid scintillator consisting of 85% trimethylborate (TMB) and 15% pseudocumene (PC), contained in a 8.5 m diameter 2.5 cm thick spherical tedlar lined acrylic vessel. TMB and PC together form a scintillator with a relatively high scintillation output of 33% that of Anthracene. The acrylic vessel will be suspended in purified light water with the PMTs, fitted with reflectors, concentrically distributed on a stainless steel geodesic structure a distance of 2 m from the vessel, all of which is contained in a plastic lined iron or steel cylinder 17 m high by 17 m in diameter. A second design option has the PMTs in air and optically coupled to a 13.5 m diameter spherical stainless steel containment vessel, with only the reflectors in water. An added 1 m thick low background sulfurcrete wall would enhance the shielding for the second option only and serve as a safety feature in the advent of catastrophic failure of the containment vessel. In either case, the 1660 20 cm diameter PMTs will provide an effective photocathode coverage of 50%.

As little as 10^{-15} to 10^{-16} g(U & Th)/g of uranium and thorium contaminants are expected in the scintillator itself, and this happens to coincide with the design goal as well. A 50 μ m tedlar coating on the inside surface of the acrylic vessel will adequately reduce the diffusion rate of ^{222}Rn from the acrylic (at an assumed purity level of only 10^{-12} g/g) into the scintillator by four orders of magnitude, effectively rendering the background contribution from the acrylic to less than one percent of the intrinsic background from the scintillator. In fact, all the detector components with the exception of the scintillator will contribute no more than 2 counts/day to the background, including cosmic ray induced events. The scintillator, on the other hand, is expected to produce 11 counts/day of background events if at 10^{-16} g[U,Th]/g, or 110 counts/day if only at 10^{-15} g[U,Th]/g. The external and internal rates together represent the total expected background levels in Borexino. The 0.25 MeV detection threshold, mentioned earlier, was essentially due to the possible background events from the beta decay of ^{14}C in the scintillator and the Compton edge for the recoil electrons effectively limits the detection of events from the 0.86 MeV ^7Be ν 's to a maximum of 0.66 MeV.

Software cuts will set the fiducial volume to 0.1 ktonnes for ^7Be measurements and 0.24 ktonnes for the equivalent ^8B search discussed below. At low energies, 0.2 MeV, the energy resolution will be 32 keV with a corresponding 35 cm spatial resolution. At a higher energy, of 1 MeV, the energy resolution is degraded and increases to 76 keV, whereas the spatial resolution is improved to 13 cm.

The expected signal rates from the SSM (without neutrino oscillations) as well as with the MSW effect folded in are on the order of 50 and 10 per day, respectively, in a 0.25 MeV to 0.8 MeV window (in a 0.1 ktonne fiducial volume.) The total background levels would be either 13 events/day or 112 events/day as outlined above. Hence, assuming Borexino realizes their best scintillator cleanliness goal of 10^{-16} g/g, the data should give a clear indication of the the probable cause of the SNP, and easily provide the first good measurement of the ^7Be neutrino flux and spectrum. The only possible signature, however, attributable to the solar origin

of the neutrinos resides in the observation of a seasonal fluctuation in intensity proportional to $1/R^2$. Such a seasonal variation is also weak at best and represents only about a 3.5% half-yearly change, again, only for the high purity scintillator case.

Besides the ^7Be neutrinos, Borexino can also investigate the lower portion of the high energy ^8B spectrum because of the natural presence of ^{11}B in the scintillator. (Eighty percent of the natural boron is the ^{11}B isotope: the remaining 20% is ^{10}B .) The fiducial volume must be increased from 100 tonnes to 240 tonnes of scintillator (containing some 22 tonnes of B) to compensate for the lower flux, and the background levels will remain acceptable since they are inherently lower in the energy region of the ^8B neutrinos. An effective threshold of 4 MeV will essentially eliminate the background events from thorium and other internal sources. Hence, Borexino will probe the ^8B spectrum from 4 MeV to the 15 MeV upper limit, effectively being the first detector to look at the lower portion of the spectrum below 6 MeV. Besides the usual electron scattering channel, ^8B events will also be detected through the ^{11}B to ^{11}C charged current reaction. The charged current reaction will lead to an expected signal of 222 events/year (92) according to the SSM (SSM+MSW) with an added signal of 364 events/year (176) according to the SSM (SSM+MSW) for elastic scattering.

The presence of ^{10}B will enable the detection of solar ν_e 's as well and permit the calibration of the detector via a suitable ^{90}Sr source. Detection of solar ν_e 's would be a good indication of Majorana neutrino magnetic moments or of neutrino decay. The major obstacle would be the low signal rate of about 20 per year above the necessary 5 MeV threshold. Background events from terrestrial radioactivity limit the useful detection threshold to 3.3 MeV and reactor born ν 's to above 5 MeV. On the other hand, ^{90}Sr $\bar{\nu}$'s can be used for calibration purposes. Sources are inexpensive, readily available, and can be made with strengths of over 5 MCi. Situated a distance of 7 m from the Borexino detector, such a source would produce a signal of 141 events/day via elastic scattering on electrons, and 80 events/day from

inverse beta-decay on the available protons. The background levels would be easily determined with an appearance-disappearance type experiment where the source would be moved to a safe distance to have its effects disappear.

Even as new detectors are being built or planned, the Homestake, KamiokandeIII, SAGE, and GALLEX collaborations are continuing to acquire data. As more detectors come online and publish new contemporary data, whether corroborating or not the ongoing results from established detectors, comparison of the results will narrow down the allowed MS parameter space. Despite what may appear to be an adequately well studied flux for example, the ^8B neutrinos have not as of yet been as well examined as the Sudbury Neutrino Observatory (SNO) proposes. Granted, Borexino will detect ^8B neutrinos of lower energy than SNO, but from the statistics point of view, SNO clearly will have the advantage. As with all groundbreaking experiments, it is desirable to have data from many detectors of different design in order to minimize the effect of unknown and unsuspected systematic errors.

Chapter 3

The Sudbury Neutrino Observatory (SNO)

3.1 What SNO Proposes to Measure and Why

H. H. Chen [23] in 1985 first suggested that a large 1000 tonne heavy water Čerenkov detector could detect the effect of neutrino oscillations on the predicted SSM flux. Chen's paper prompted a group of scientists from the United States, Great Britain, and Canada to pool their efforts and produce a viable proposal in 1987 [28] for such a detector. After less than three years of relentless lobbying, the Sudbury Neutrino Observatory was finally fully funded in January of 1990. In part, successful funding was achieved because of the cost savings attributed to the availability of the required 1 kt of heavy water (which could be borrowed from AECL), and also due to the active mine where the detector would be located, namely INCO's Creighton Mine in the municipality of Walden, near Sudbury, Ontario.

The Sudbury Neutrino Observatory proposes to measure only the ${}^8\text{B}$ ν 's, as mentioned earlier, simply because of the 6 MeV threshold dictated by the expected high background levels (discussed in more detail below.) The ${}^8\text{B}$ ν 's are born of the ${}^8\text{B} \rightarrow 2\alpha + \beta^+ + \nu_e$ reaction in the p-p chain which occurs for only 0.01% of all p p

events. Neutrinos of energy up to a maximum of 15 MeV are produced with a flux at Earth of $5.8(1 \pm 0.37) \times 10^6 \text{ cm}^{-2}\text{s}^{-1}$ [12] and expected signal on a deuterium target of $6.01(1 \pm 0.38) \text{ SNU}$ (0.02 SNU are from the pep reaction, a variant of the initial p-p reaction.) For the most part, and as evident above, the major source of uncertainty stems from the calculated ^8B flux.

There are three basic reactions by which solar neutrinos are detected in SNO:

$$\nu_x + e^- \rightarrow \nu_x + e^- \quad (3.1)$$

$$\nu_e + d \rightarrow p + p + e^- \quad (3.2)$$

$$\nu_x + d \rightarrow p + n + \nu_x \quad (3.3)$$

Equation 3.1, referred to as the Elastic Scattering (ES) reaction, can detect all three neutrino flavours with rates according to the cross-section, and is detected by the Čerenkov radiation given off by the relativistic recoil electrons. Equation 3.2, the inverse beta decay of the deuteron known as the Charged Current (CC) reaction, is so named because it is mediated by the charged W^- vector boson. Its signature is again via Čerenkov radiation from the electrons. The last reaction listed above, equation 3.3, is referred to as the Neutral Current (NC) reaction since it is mediated by the neutral Z^0 boson. The delayed capture of the neutron which emits a gamma ray serves as the signature for the NC reaction, and also suggests the necessity of the addition into the heavy water of a high neutron capture cross section element.

The elastic scattering reaction of equation 3.1 affords no threshold except for the Čerenkov limit, but is nevertheless effectively limited to a minimum of 6 MeV in order to avoid most of the gamma background radiation, from detector components and external sources, which mimic a ν - e^- elastic scattering event. All neutrino flavours can undergo ES, although ν_e have a reaction cross-section greater by 6 or 7 times that of ν_μ or ν_τ because of the extra charged current channel available. The expected signal rate (above a 5 MeV threshold) can be found in table 3.1 [28, page

Model and Effect	CC	ES	NC
Standard Solar Model	9750	1100	2800
Vacuum Oscillations	3260	480	2800
Matter Oscillations $E_c=9$ MeV	3750	645	2800
Matter Oscillations $E_c=2$ MeV	98	173	2800
SSM Wrong: Flux 2×10^6 cm ⁻² /s	3255	360	933

Table 3.1: The expected signal rates in SNO for various reactions with and without the added effects of various new physics solutions to the SNP including MSW oscillations. A minimum energy threshold of 5 MeV and interaction on Cl is assumed for the NC predictions. The numbers shown are for a threshold of 5 MeV for one kilotonne-year of data.

28] below.

A threshold of 6 MeV would undoubtedly imply a small reduction in the numbers quoted in table 3.1, but the implications of the data would remain the same. The recoil energy of the electron should closely follow the initial energy of the neutrino as evident in the Kamiokande results. The energy spectrum wouldn't be well measured, on the other hand, with the above low ES statistics, but because of the directionality of the recoil electrons, the solar origin of the signal would be demonstrated. The recoil electrons are kinematically constrained to the direction pointing away from the Sun thus proving the signals solar origin. Despite the fact that the ES reaction also occurs in the heavy water, its measurement would be carried out in a pure light water envelope surrounding the heavy water, where a purer signal could be obtained. The ES reaction component in the heavy water cannot be unambiguously separated from the CC signal despite the directionality of the ES events.

On the other hand, the CC reaction recoil electrons carry the neutrino spectrum information because of the large relative mass difference between the produced particles. The energy of the incident neutrino is related to the electron energy by $E\nu=1.44+E_e$ MeV, where the 1.44 MeVs of energy is the sum of the reaction threshold energy and the energy imparted to the protons. As with the ES electrons,

the Čerenkov radiation that the CC electrons emit can be collected by the array of PMTs. The energy of the event is then related to the number of PMT hits (loosely distributed in a single or double superimposed ring pattern [20].) Because of the several thousand CC events per year expected (see table 3.1 above), the statistics for the ${}^8\text{B}$ neutrino energy spectrum will be very good. CC electrons are expected to be directional with a two to one forward to backward asymmetry. A measurement of the events pointing back towards the Sun would imply that twice that many pointed away from it and are due to the CC reaction. Since the ES electrons are all forwardly constrained, a simple subtraction is possible, although such a procedure would only produce integrated flux results, and would be dependent on the uncertainty of both the CC and ES fluences.

Once the CC neutrino energy spectrum has been measured, it can be compared with the predicted SSM spectrum and any differences in spectral shape could be indications of neutrino oscillations. The three types of oscillation solutions would give rise to differing effects on the spectral shape. The large mixing angle solution (the rightmost vertical portion on an MS diagram, and is also an adiabatic solution) which uniformly affects the neutrino flux virtually regardless of energy, produces a spectrum of similar shape but of lower amplitude. Vacuum oscillations would produce very similar spectra, hence SNO data wouldn't allow the separation of the two solutions, but would nevertheless indicate oscillations. The main adiabatic solution (or horizontal portion of an MS diagram) affects only the high energy neutrinos above about 7 MeV of which few survive as ν_e 's, hence would produce effects similar to the large mixing angle on the observed neutrino energy spectrum. Because SNO is limited to energies above 6 MeV, differentiation between these two classes of solutions would be difficult. The third possible solution is nonadiabatic, the diagonal portion of the MS diagram. Low energy neutrinos are preferentially converted under nonadiabatic conditions, hence SNO would detect no change in the predicted spectrum. Neutrino decay only affects low energy neutrinos as well, thus an intact high energy ${}^8\text{B}$ spectrum in SNO would be an indication of either neutrino

decay, or nonadiabatic neutrino oscillations.

The neutral current reaction, which is literally the disintegration of the deuteron, has a threshold of 2.223 MeV and is flavour blind. No information other than the total flavour-blind solar neutrino flux can be obtained from this reaction since the neutrino only scatters off of the deuterium nucleus causing its dissociation. The signal is detected when the neutron is captured on a ^{35}Cl nucleus which subsequently emits a >6 MeV gamma (53% of the time) visible to the PMTs [29]. The Cl is supplied by NaCl which is added at the 0.25% level (2.5 tonnes) to the heavy water. Although research is presently underway evaluating MgCl_2 as additive (at the 0.20% level), NaCl remains the default option unless MgCl_2 is ultimately shown to be equivalently acceptable or superior. An alternative NC enhancement technique which would complement the salt measurements was also developed which employs ^3He filled nickel cylindrical proportional counters (PC) deployed in an array formation in the heavy water. The nickel PCs would not be deployed at the same time salt was present in the water, however. In either case, the ratio of NC (total flux) to CC (ν_e only flux) would immediately reveal any oscillation effects, and would require an alternation between salt-in and salt-out operation modes, unless the CC and NC peak separation was sufficient to allow for simultaneous CC and NC measurements. The one proof of new physics, therefore, lies in the NC/CC ratio, thus, a good measurement of the NC flux is paramount to SNO's success or failure.

The signature, for the NC reaction, is not unique because of two dangerous gamma rays: a 2.615 MeV one (36% of all decays) from the end of the ^{232}Th chain, and similarly a 2.445 MeV one ($55 \times 2.8\%$ of all decays) from the ^{238}U chain. Both gammas are above the photodisintegration threshold for deuterium and would produce mimicking neutrino events indistinguishable from true neutrino events. The design criteria, for the background upper limit of 10% of the solar signal, effectively dictates the maximum allowable ^{238}U and ^{232}Th levels in all detector components. In the heavy water, where the requirements are the most stringent (since it is the core of the detector), the design calls for tolerances of no more than 3×10^{-15}

$g(\text{Th})/g(\text{D}_2\text{O})$ and $g(\text{U})/g(\text{D}_2\text{O})$. Thus, due to the great importance of the NC flux for SNO, the NC background must obviously be well known and controlled. Hence, the determination and monitoring of the NC background is the focus of chapter 5.

Of interest as well, are the hep neutrinos (from the ${}^3\text{He}(p, \nu_e e^+) \alpha$ reaction) which have a spectrum endpoint energy of 18.77 MeV. Only ${}^8\text{B}$ and hep neutrinos have a portion of their energy spectrum above the 6 MeV threshold for SNO, although the SSM flux predicted for hep neutrinos is considerably less than that for ${}^8\text{B}$ by almost three orders of magnitude. Despite the lower flux, hep neutrinos above an energy of 13.5 MeV [12] are expected to produce 10 events/kt/yr via the CC reaction (provided oscillations do not reduce the number), whereas ${}^8\text{B}$ neutrinos above the same energy threshold would produce only 2 events/kt/yr. At energies above 13.5 MeV, the ES and background levels would be negligible. Of all the solar neutrino sources, the hep reaction is the least sensitive to the core temperature of the sun. The measurement of its flux could possibly help shed some light on the SNP.

The effect of non-standard neutrino physics and solar models will be evident in SNO data as shown in table 3.1. The NC reaction will easily determine if the SSM is at fault or not if the rate is significantly less than the 2800 events per kt-y expected. CC and ES event totals are seen to vary as well, for two energy thresholds, depending on the applied effect. Of equal importance are the effects on the ν_e spectrum as mentioned earlier.

Electron anti-neutrinos, although not normally produced by the Sun (according to the SSM), are copiously produced by Supernovae, and would also be detectable in SNO via the following two reactions:

The reactions of equations 3.4 and 3.5 would produce one or two (respectively) NC type neutron capture events followed by a photon with a minimum energy of

1.02 MeV from the annihilation of the positron. Because of the dynamics of stellar collapse, a large neutrino signal would be detected over a short period of time on the order of several seconds. Such a prominent flash of sudden activity in SNO would therefore be unmistakably due to a supernova. This would give advance warning permitting the observation of the supernova by optical means.

3.2 The SNO Detector Design

3.2.1 The Structure of The Detector

The background level design goal of the SNO detector is to limit the background noise to 10% of the expected NC signal rate. The goal can be achieved if all the components in and around the detector are well chosen for their high radiopurity and further purified if necessary. Each component, down to the glue used on the acrylic vessel, would have to be screened and tested thoroughly before any decision could be made as to its final use.

SNO scientists have designed the Sudbury Neutrino Observatory with the control of the various sources of background in mind. As previously stated, the observatory is situated far beneath the surface of the Earth, 2.07 km underground for 5900 mwe, to render the μ flux induced background negligible at 1.5 detectable spallation events per day for the 1 kt of heavy water. The rock cavity that houses the SNO detector has been built according to the maximum allowable dimensions determined by long term stability measurements performed by INCO engineers. With its 25 m diameter and 34 m height, the cavity is the largest unsupported open underground excavation in the world. The detector is situated about one kilometer from the number 9 shaft in the mine, which is still active and will continue to be for at least the next 20 years, thus separating it from the mining activity. The fact that the mine is still active ensures continued access and services to the SNO site for the duration of the project.

The detector itself, see figure 3.1, consists of 1 kt of ultrapure heavy water (which is $>99.85\%$ isotopically pure) contained in a 5 cm thick, 12 m diameter spherical acrylic vessel (AV), buoyed up by 7,500 tonnes of ultrapure water (UPW). Kevlar ropes, suspended from the structural steel deck, also help keep the acrylic vessel suspended in its place and are attached at the equator by an acrylic ring bonded to the vessel. The 9450 20 cm Hamamatsu R1408 PMTs, providing 40% photocathode coverage, are located 2.5 m away from the acrylic vessel and supported by an anodized aluminum geodesic support structure. Each PMT is fitted with a coated anodized aluminum reflector that enhances their light collection efficiency. The holes in the entire PMT support (PSUP) structure will represent only 1% of the surface area in order to prevent the exchange of water between the volumes inside and outside of the PSUP, in other words the PSUP will be 99% water-tight. Such a measure will ensure that the dirtier water exterior to the PMTs will not mix by convection with the cleaner water forward of the PMTs.

The walls of the cavity are covered with a steel wire mesh and rock bolted before a thick coating of shotcrete is applied. Shotcrete is a specially formulated concrete which can be applied to vertical or overhanging surfaces by spraying. A drainage mesh in 15 cm strips is distributed over the entire surface and covered with more Shotcrete. The final layer of the detector outer casing is a double Urylon coating of about 6.4 mm that is watertight and consists of a thick layer and a much cleaner thin layer on top. The liner also serves to reduce the flux of radon atoms into the water. Also of concern is the 12% loss of the photoelectron collection efficiency on some of the PMTs because of the Earth's magnetic field (horizontal component of 0.15 Gauss, vertical component of 0.55 Gauss.) In order to minimize the effect of the Earth's magnetic field on the PMTs, a series of 14 horizontal current carrying wire loops are imbedded in the Shotcrete which, when active, counter the vertical component of the Earth's field leaving a maximum of 20% of the original field. The net effect reduces the efficiency loss to a maximum of 3% on some of the PMTs.

Above the water level, a steel deck (attached to the rock walls) provides access

Figure 3.1: The Mark II design of the Sudbury Neutrino Observatory detector. The 1 kt of heavy water is contained in the spherical acrylic vessel at the center which is enclosed by the geodesic structure which supports the PMTs. The entire structure is suspended in light water which fills the volume of the cavity.

to the central pipe leading down to the acrylic vessel, and provides a sealed environment above the water level where the mine air will be replaced with boil-off nitrogen gas. The nitrogen cover gas will be constantly displaced with clean nitrogen to purge it of the oxygen and water vapour trying to reach equilibrium from the water. It will prevent the water from coming in contact with mine air, which cannot be employed because of the high radon levels (2 pCi/l as opposed to surface room air at 0.1 pCi/l), and prevent oxygen from being redissolved into the pure water, which will be degassed, since muon spallation requires ^{16}O . The access provided by the deck will permit the lowering of calibration devices, as well as water inlet and outlet pipes, into the heavy water.

The high water purity for SNO will be achieved with two similar but separate systems, one for each type of water. The light water system mainly consists of an iron removal stage with multimedia filters (which contain packed beds of particulate matter of various sizes) and 10 μm filters followed by two or each of activated charcoal filters, sodium zeolite softeners, and cartridge filters. All these initial steps are required to prepare the INCO water for more sensitive equipment by removal (filtering) of solids of a certain size and also by replacing divalent elements with monovalent elements (called softening). Once the water has been pretreated as above, three reverse osmosis (RO) systems purify the water in a cascade formation: the concentrate of the first RO being treated by the second, etc.. The subsequent stage consists of an Ultrafiltration (UF) membrane, a water chiller (since the desired detector operating temperature is 10°C), de-ionizers, and two ultraviolet units of different wavelengths, one each on the input and output of the next stage: the process degasser. The towering process degasser removes ^{222}Rn which has made its way into the water either from contaminants that were already present in the water, or by diffusion through the walls of the hundreds of meters of polypropylene pipes or through the cavity liner. The extracted radon is then expelled into the mine air away from the personnel access areas. Prior to its return to the cavity, the water must also be assayed to determine its purity and expected background contribution.

A choice of three types of monitoring systems are available: a monitor degasser, dual MnO_2 columns, and an Ultrafiltration unit (followed by a $0.2 \mu\text{m}$ filter). The extracted radon and water vapour mixture is separated with the help of a cold vapour trap. Radon then is further separated from any residual water vapour by two stages of radon cold traps in series. The secondary radon trap can then be emptied into Lucas cells for detection of the signals from radon and its daughters.

The water intake pipe for the light water purification system is located near the surface and cavity wall. The cleaned water supply is first piped to three points inside the PSUP, one on each side at the equator and the third at the base, then to four points around the outside of the PSUP: one on each side at the equator and at the lowest point at the base, and one close to the floor of the detector, below the base of the PSUP. The four chilled water return points are situated along the cavity walls at two different levels. In essence, the water destined to be cleaned is taken from near the light water surface, close to the cavity wall, and is returned, once clean, inside the PSUP. Chilled clean water is also returned to the cavity in the center of the body surrounding the AV. The net effect is the flow of clean water from in front of the PSUP to the outside of it, preventing any inward flow of contaminants. The monitoring intake pipes, of which there are five, are all but one distributed inside the PSUP. They straddle, in pairs, the meridian of each hemisphere of the PSUP with one intake near the PSUP inner surface and the other close to the AV. The intake external to the PSUP samples the water where the PSUP connects with the neck of the AV.

The heavy water system essentially employs similar equipment as listed for the light water system. The major components are cation exchange beds and a multi-stage RO system. A UV system is not necessary since heavy water doesn't support biological growth. Process and monitor degassers are also part of the heavy water system. Many access points from which samples could be obtained for monitoring of ^{232}Th and ^{238}U concentrations are also an integral part of the system. An added ultrafiltration stage just prior to the water return will catch any fines which may

have been introduced into the water by the purification system. A complete and detailed explanation of the heavy water system, which is of more direct interest than the light water system, will be discussed in more detail below.

The various water systems and electronics are all situated at the SNO site in the mine in drifts off of the main SNO drift. These areas contain all the water purification equipment, the data acquisition system, and crew facilities since access to the surface is limited to three times a day during shift changes only (the elevator cages are used to carry personnel and equipment to the surface the rest of the time.) Because the mine environment is such a dirty and dusty one, it is necessary to isolate all SNO areas from the mine. The air must be filtered before being circulated in the SNO drifts and all personnel must change and wash before entering the work areas to eliminate the dust influx from human carriers.

3.2.2 Sources of Internal and External Backgrounds

In order to achieve the low background levels required for SNO, the contribution from absolutely all the components of the detector, no matter how seemingly insignificant, had to be known. All candidate detector components and materials had to be thoroughly tested: only those with satisfactory low levels of radiocontaminants, and which could be produced with adequate quality assurance, were chosen. Since the detector is essentially a water Čerenkov counter, all γ or β sources susceptible to produce coincidences with energies above the expected 6 MeV PMT threshold, had to be known. As for the NC reaction, photons of energy greater than 2.223 MeV or neutrons constitute the background. As mentioned earlier in part, the main elements capable of producing radiations of the above type and energy are ^{40}K , ^{232}Th , ^{235}U , ^{238}U . The two most important chains are those of ^{232}Th and ^{238}U which produce α and β particles along with the two most troublesome photons, at 2.615 MeV (^{232}Th) and 2.445 MeV (^{238}U) (figures 3.1 and 3.2). All detector components must have low enough levels of these elements to satisfy

the total background requirement. The closer to the heavy water fiducial volume that a given component must be, the cleaner it must be, with the heavy water itself having to be the cleanest part of the entire detector. Ultimately, the final product will be the worlds lowest background facility.

The rock (Norite) where the SNO detector is situated contains 3.3×10^{-6} g/g of ^{232}Th and 1.2×10^{-6} g/g of ^{238}U . As outlined earlier, both decay chains give rise to γ 's of energy greater than the NC threshold of 2.223 MeV. Their daughters also produce α particles which can produce γ 's and free neutrons, via $(\alpha, p\gamma)$ and (α, n) reactions on light elements such as ^{28}Si , ^{30}Si (30% total), ^{27}Al (9%), ^{25}Mg , ^{26}Mg (3.3% total), and ^{23}Na (2.2%), all of which are present (as indicated by the percentage by weight) in the Norite. The capture of the neutrons produced above, and those from spontaneous fission, both yield γ 's of up to 10 MeV and therefore constitute, along with the remaining flux of uncaptured neutrons, a source of background for the NC reaction. The same γ 's also contribute to the ES and CC reaction backgrounds because they can Compton scatter with electrons.

Radon gas, namely ^{220}Rn ($t_{1/2}=55.6$ s) and ^{222}Rn ($t_{1/2}=3.82$ d) from the ^{232}Th and ^{238}U chains respectively, emanates from the rock walls and can make its way to the light water. Although the liner structure is sufficient to virtually eliminate the ^{220}Rn component because of its short half-life, the flux of ^{222}Rn , on the other hand, can only be reduced to an acceptable level with the appropriate liner design, hence the necessity to degass the light water. Such a measure against radon is necessary because the gas's mobility brings the atom closer to the core of the detector before it decays. The subsequent 2.445 MeV gamma ray from the ^{214}Po radon daughter is therefore produced in closer proximity to the heavy water and has a greater chance of penetrating into the fiducial volume or contributing to the ES and CC backgrounds.

The other components of the detector, namely the PMT cables and reflectors, and the AV and its cables, must also be of a certain purity to avoid contributing substantially to the background levels. Also, additives, such as NaCl or MgCl_2 ,

Figure 3.2: The ^{232}Th decay chain. Note the 2.615 MeV γ ray at the end of the chain.

Figure 3.3: The ^{238}U decay chain. Note the 2.445 MeV γ ray near the end of the chain.

Detector Component	^{232}Th g/g	^{238}U g/g
Heavy Water	3.0×10^{-15}	3.0×10^{-15}
Light Water	3.0×10^{-15}	3.0×10^{-15}
Acrylic	2.5×10^{-13}	3.0×10^{-12}

Table 3.2: The desired levels of ^{232}Th and ^{238}U for various detector components in grams per gram of material.

must have a negligible effect on the background levels. The desired radiopurity levels for the major detector components can be found in table 3.2 below. For each component, candidates were proposed all of which were tested for their ^{232}Th and ^{238}U content by SNO gamma analysts. More often than not, the material with the lowest levels remained unacceptable, at which point further study of the manufacturing process would reveal which additive was the greatest contributor to the background levels observed. With the cooperation of manufacturers, it was possible to eliminate or substitute additives to design a compound of the required properties and background levels needed for SNO use.

Despite the high purity levels the components will have, leaching of ^{232}Th or ^{238}U and emanation of ^{220}Rn and ^{222}Rn into the light and heavy water will always occur. Water molecules are polar and tend to dissolve most substances they come in contact with and this is obviously also true of ultrapure water. During the construction phase of the project, dust deposition on all components must also be controlled, whether it be during transport from the surface or installation (not to mention during manufacture.) Thus all components must be manufactured clean and kept so at all subsequent times otherwise the dust will be dissolved by the water during the initial fill and raise the background levels accordingly. Despite all efforts to prevent or remove accumulated norite rock dust on both AV surfaces, a certain amount will remain which must not exceed 2.2 g. The 2.2 g contains $7.4 \mu\text{g}$

of ^{232}Th which gives rise to one neutron per day in the D_2O .

With the constant inflow of contaminants previously outlined, it is clear that the water behind the PMTs, which contains all the PMT electronics, wiring, and is in contact with the liner, will always have a higher concentration of leached contaminants than the water ahead of the PMTs (which sees only the AV outer surface and the PMT glass.) The purified water return is in front of the PMTs with the water intake from behind the PSUP. Such an arrangement will ensure that convection will not mix the dirtier water outside the PSUP with the cleaner water in front of it provided the PSUP is 99% water-tight. This is necessary if part of the water between the PSUP and the AV is to serve for data acquisition for the ES reaction. It will be necessary to take into consideration the convection patterns of both waters with respect to the intake and outlet points for the water purification systems to avoid purifying only a portion of the water at the expense of the rest, or from the point of view of contaminant transport. Care must also be exercised with the removal and return of the heavy water to ensure proper circulation and mixing.

There is one last source of contamination which must be dealt with: bacterial growth of any kind. Obviously, bacterial growth cannot be allowed to occur unchecked, otherwise everything will be coated with growth, rendering the water murky and the AV opaque. Under those conditions, the water would no longer have optimal transmittance for the Čerenkov photons, and this would greatly affect the results. By degassing the water, as stated earlier, and keeping it under a pure nitrogen atmosphere, aerobic bacteria can be controlled. Since the detector will also be kept at a temperature of 10°C (rock walls are at 41°C) and in total darkness, anaerobic bacteria can also be controlled. During the cleaning stages of the components, before they are shipped down to the cavity, a bactericide will also be employed along with the dust removal cleaning procedure.

3.3 The Importance of Pure Light and Heavy Water

The various cavity liner materials and the norite rock produce similar radiations since they contain the same trace radiocontaminants. Unhindered, the γ and neutron flux would ultimately flood the heavy water and swamp the PMTs with background signals far greater in number than the expected solar neutrino signal. The resultant neutron and high energy γ ray flux must therefore be reduced, and such is the role of the light water fill. Through neutron capture on ^1H , the neutron flux will be virtually eliminated since the emitted 2.223 MeV γ ray will lose energy by Compton scattering before entering the heavy water. A fission neutron will typically be thermalized after travelling a distance of 14 cm in water and be subsequently absorbed after a further 7 cm. The 4 m of water before the PSUP and the 2.5 m after it are sufficient to virtually eliminate the neutron background signal from the rock and liner. The same applies to the PMTs since they are located 2.5 m from the AV. The remaining γ flux from all external sources, the norite and liner materials, will also be attenuated in the light water because of the attenuation coefficient of 3 m^{-1} . The flux from the rock and liner combined is 36 photons per day above threshold at the PSUP surface, 0.4 per day 1 m away from the AV, and 0.02 at the AV surface. The corresponding flux originating from the PMTs and the PSUP is expected to be 120 per day which translates to 1.6 per day 1 m from the AV and 0.08 per day at the AV. The total flux 1 m from the AV is therefore 2 photons per day (above a 5 MeV threshold) and 0.1 per day at the AV. Compared to the already negligible μ spallation event rate, the photon NC background rate is very small. Due to its low photon flux at 2 per day, the 1 m of water adjacent the AV can also be used to detect electron neutrinos, although only for the ES reaction.

The light water itself must also be purified to reduce the amount of ^{232}Th and ^{238}U present (table 3.2.) Although the same initial radiations are produced, only trace amounts of the elements necessary for conversion (via $(\alpha, p\gamma)$ or (α, n) reac-

tions) abundantly present in the norite are available in the water. The only remaining sources of background radiation are the β and γ rays. Due to their proximity to the PMTs, the Čerenkov light they produce could be confused with ES or CC events. Hence, their flux must be reduced which can only be achieved by extracting thorium and radium from the water and also by degassing for reduction of the ^{222}Rn daughter. The procedures and difficulties for thorium and radium extraction are the subject of section 3.4 below.

The heavy water, on the other hand, must have much lower concentrations of U and Th as listed in table 3.2 since it is the heart of the detector. Photons of 2.615 MeV from the ^{232}Th chain have a deuteron photodisintegration and Compton cross section of 1.2 and 125 millibarn (mb) respectively (the barn is a unit of cross section equal to $1 \times 10^{-24} \text{ cm}^2$). Since for every heavy water molecule there are two deuterons and ten electrons, and allowing for 11.5% of the Compton scattered photons with sufficient residual energy to also cause photodisintegration, the ratio of Compton events to photodisintegrations of the deuteron is 470 to 1. Thus one free neutron is produced for every 470 photons. At equilibrium, about 130 photons (2.615 MeV) are produced per μg per day, which implies that a quantity of 3.7 μg of ^{232}Th gives rise to one free neutron per day in the 1 kt of heavy water, hence the required radionuclei purity level of $3 \times 10^{-15} \text{ g(Th)/g(D}_2\text{O)}$. The 2.445 MeV photon from the uranium chain has comparable cross sections at 0.8 and 130 mb, respectively. Allowing for the 7.2% of Compton scattered photons capable of photodisintegration, the ratio of Compton to photodisintegration events is 750 to one. At 16.8 photons per μg per day, the concentration of uranium responsible for one free neutron per day in the 1 kt of D_2O is 45 μg , which implies a minimum purity limit of $4.5 \times 10^{-14} \text{ g}(^{238}\text{U)/g(D}_2\text{O)}$. Since the original proposal in 1987, the maximum uranium limit has been lowered to $3 \times 10^{-15} \text{ g/g}$ after it became apparent that such a level could just as easily be reached.

In order to maintain these low radionuclei levels, the water must be constantly purified since the influx of contaminants is relentless from all sources. Of great

importance as well is the monitoring of the radionuclei levels in both light and heavy water. To understand the background well, its level must be reliably measured at regular time intervals with sufficient sensitivity. Such is the focus of the next section and of Chapter 4.

3.4 The Assay of Th and U Chains via Radon

The heavy water purification system is equipped with several access points consisting of pipes running along and near to the AV inner surface and distributed at semi-regular vertical intervals (at elevations of 12.0, 15.2, 19.6, 22.4, 27.7, and 28.0 m from the floor of the detector.) The first four access points approximately span the 12 m diameter of the AV, and the last two are situated in the neck of the AV. Any one of these lines can be accessed by any one of the Radon monitoring systems.

Experience from seawater radium analysis by column extraction on MnO_2 coated porous beads has proven useful in that the same knowledge can be applied to the extraction of radium for SNO [59], even with the presence of a salt additive during NC runs. Basically, the columns are cylindrical polypropylene casings containing an appropriate volume of MnO_2 coated porous beads. The bead volume required depends on the desired residence time of the water. Sufficient time must be allotted for the radium to complex with the MnO_2 , hence the amount of beads depends on the column length and the flow rate of the water. Because the size of a column is generally one liter or more, the capacity of the beads to absorb and retain radium is never a concern due to the minute amounts of radionuclei in question. The optimal type of MnO_2 coating to be employed in SNO is still, at the moment, under investigation.

All monitoring techniques, with the exception of the lead assay, rely on the MnO_2 columns, hence the necessity for its thorough understanding. Once the radium has been collected onto the MnO_2 (with a 90% or greater efficiency), after passing a large volume of water through the column, the column and beads must be dried.

The drying is achieved, after removal from the monitoring loop, with the flow of heated 60° C dry nitrogen through the column for several hours (the nitrogen is also returned to the D₂O recovery system). The MnO₂ volume when wet is 1 l, and when dry it reduces to 220 cc. Once the column is ready and dry, it can be coupled to the various counting systems discussed below. Two different methods of extraction may be employed at this point: either the radium is eluted off of the MnO₂ directly, or the radium's radon daughter, which will naturally emanate from the beads, is carried away by vacuum or in a clean nitrogen gas flow directly into the counter. In either case, there are different efficiencies associated with each step as outlined in the appropriate monitoring discussions on Electrostatic, Cryostatic, and Lucas Cell systems.

The cryodetector, a brainchild of SNO collaborators from Queens University [22, 21], was developed for ²²⁸Th monitoring by detecting the alpha activity of the ²²⁰Rn daughters after the radon has been transported from the MnO₂ column. Beforehand, the column would sample 20 to 100 tonnes of D₂O (at flows of 20 to 100 lpm for 8 to 24 hours). The operation of the detector is simple. Initially, the ²²⁰Rn must emanate from the MnO₂ coating, which it does with 70-75% efficiency, and it is carried off by the nitrogen gas flow with a transfer efficiency of essentially 100%. A recirculation pump serves to circulate the nitrogen gas at 30 lpm or less at 1 to 50 Torr pressure through 3/8" tubing. The detector itself consists of two facing Si PIN diodes (2.8 cm by 2.8 cm) of 300 micron thickness each (a bias of up to 30 V is applied to them via battery). In order to avoid having problems with residual humidity from the columns, the nitrogen carrier gas first passes through a water trap at about 170 K. Radon was shown not to condense at that temperature (radon begins to condense only below 120 K). The cryocell (diode array) itself is kept at an optimal 77 K where it was shown that the trapping efficiency is maximal at 100% as well. Finally, with the radon atoms in view and decaying away naturally, the diodes can detect the α particles with a geometrical efficiency of 47%. Since all the α 's from the decay of radon and its daughters are detected with the

same geometric efficiency (ϵ_{geom}), an overall counting efficiency (ϵ_{count}) is therefore appropriate and is calculated to be 85% from the probability of missing a radon decay $(1 - \epsilon_{count}) = (1 - \epsilon_{geom})^3$. Combining this with all the other efficiencies listed above ($85\% \times 75\% \times 100\% \times 100\%$) yields the total efficiency of the technique to be 64%. In addition, coupled to the 64% efficiency of the technique is the initial efficiency for extraction of the radium onto the MnO_2 .

The background levels for the system were shown to be 2 Rn atoms per day. During a monitoring session, an MnO_2 column would be sampled by the Cryodetector for a period of 15 to 20 days. At the desired 3×10^{-15} g/g Th level in the D_2O , the Cryodetector would see, in the first day of counting, a signal of 4.5 counts (with an additional 2 counts for background) and would see, after 20 days of counting, a signal of 25.5 counts (with an additional 40 counts from background on average). In essence, the Cryodetector is sensitive enough for use in SNO as a ^{232}Th monitoring technique.

The second radium/radon based monitoring technique, the Electrostatic counter [68], relies on the same column extraction and drying procedure used for the cryogenic system. The counting system, developed by SNO collaborators at the University of Guelph, also relies on the transport of radon atoms in a nitrogen gas flow under low pressure. The actual detector is a windowless Si Surface Barrier (SSB) detector isolated from the chamber walls where it is mounted. A potential difference applied between the SSB and the chamber walls produces an electrostatic field which carries positively charged ions towards the SSB. All the radon daughters produced are largely positively charged and would migrate to the detector, therefore increasing the chances of detecting the emitted α particle. A cryotrap eliminates all of the unwanted residual water vapour from the column drying stage in a similar fashion as is done with the Cryodetector. The alpha spectrum is recorded every three hours so that a count versus time spectrum is obtained. The advantage here lies in the ability to distinguish between radon that has emanated from the column and radon that has been introduced during the drying stage, thus eliminating the

effect of a background source.

The ultimate background levels achieved were 0.5×10^{-15} g/g of Th for an equivalent 100 tonne D₂O sample and 0.2×10^{-15} g/g U for the same sample size. The combined two peak detector efficiency is 40%. Ultimately, the detector uncertainty is under 10% (statistical) and about 15% total at the 3×10^{-15} g/g U and Th which, although a little higher than the 10% desired, is sufficient to allow good assays of the heavy water.

The last monitoring technique, developed again at Queens University, which relies on radon is the Lucas cell detector [43]. Radon for the Lucas cells is obtained from a cylindrical acrylic emanation chamber (65 cm by 30 cm outer diameter) which contains either MnO₂ beads or any material for which the radon level is desired. Lucas cells are simply scintillator coated (silver-activated ZnS(Ag)) acrylic hemispheres (20 cm² total surface area) which are fitted to a 5 cm diameter PMT for the detection of the light signal. The emanated radon from a sample of material can thus be isolated from other trace gases before being counted. This is achieved with two liquid-nitrogen cooled traps in series. The primary trap, which is much larger, also retains most of the traces of these other gases (Oxygen and Nitrogen) as well as any water vapour. By carefully heating the primary trap, the radon gas can be boiled off while leaving behind the other gases (which have higher boiling points) and pumped to a smaller secondary trap. The secondary trap further purifies the radon sample before it is allowed to enter the scintillator by free expansion. The ZnS coating of optimized thickness (10 mg/cm²) produces a signal in the PMT which is clearly above the PMT noise for a typical α particle energy of 5 MeV, thus rendering true α signals easy to detect.

Contributions to the background from cosmic rays and the cell acrylic are negligible in comparison to that from the natural radioactivity in the ZnS coating. For example, the acrylic (even at 100 ppt U) would only give rise to less than one count per day, whereas the residual air left in the cell (at a pressure of 200 mTorr) contributes only 0.06 cpd. Liu et al also mention that the signals from β or γ of

natural origin do not give rise to detectable signals. The ZnS itself, on the other hand, produces 3 cpd of background. Analysis of the entire system from emanation chamber to the cell has shown that the ultimate low background is 20 cpd, where 12 were from the chamber, 5 from the traps etc., and 3 from the cell itself. The efficiency for each step of the technique was found to be as follows; $72 \pm 5\%$ efficiency to pump the Rn out of the emanation chamber (containing the MnO_2 column) and into the primary trap, $75 \pm 5\%$ to transfer the Rn from the primary to the secondary trap and subsequently into the cell, and $62 \pm 3\%$ for the detection of the alpha particle once the radon has reached the cell. The overall efficiency is therefore $33 \pm 4\%$ based on the above numbers.

The background levels would be determined by the various monitoring techniques discussed above, or by the lead assay technique, before they are subtracted from the total signal detected in SNO. SNO will rely heavily on these techniques to be able to confidently extract the neutrino data. All the techniques must therefore sample the light or heavy water from certain strategic portions of the water bodies. In the next section, the heavy water system in which the monitoring techniques are an integral part is discussed in detail.

3.5 The Heavy Water Purification System

The chemical properties of heavy water, under most conditions, remain the same as those for light water, which is to be expected since chemical properties are essentially governed by the valence orbital electrons. Since the only difference between heavy (D_2O) and light (H_2O) water is the extra neutron in each deuterium nucleus, the waters mainly slightly differ in density and viscosity, and thus, the same purification technology can be applied to heavy water. All the essential components of the heavy water purification and monitoring system are shown in figure 3.4 below. Because the heavy water is on loan from AECL and it is otherwise expensive, SNO cannot afford to put any appreciable amount of it to drain, hence the absence of drain

connections in the heavy water system! What is also not shown in the system below is the nitrogen cover gas system and connections for all tanks and equipment which require it for the recovery of D_2O vapors (not to mention avoiding contact with air). In order to keep the schematic simple such that an understanding of the operation is possible, all valves, pumps, and meters of all kinds have been omitted.

The most appropriate plan of attack to reach the goal of 3×10^{-15} g/g ^{232}Th would be to attempt the removal the thorium itself, thus avoiding the production of its daughters as much as possible. The acrylic vessel itself and the dust deposited on its surface and in the bonds during its assembly will contain certain levels of thorium. The main goal of the heavy water system is therefore to remove as much thorium as possible and to allow for monitoring of the radium, radon, and lead daughters as a means of verifying the purity level achieved.

There are several main tasks which the D_2O system must perform; initial purification and fill, recirculation, degassing of ^{222}Rn and its monitoring, salination and desalination, high flow column assay, Ra assay, and Pb assay. There is considerable overlap in the use of portions of the RO system for all the types of processes. The assay modes based on reverse osmosis can be operated simultaneously with or without any of the assay modes, although the high flow columns do require the RO to be operational. Each process is outlined in detail as follows.

During the initial fill, the heavy water must first of all be transported down to the detector site, and this is achieved with 3.5 to 5 tonne rail tankcars; they are filled at the surface from the stainless steel road tanker trucks whence the D_2O was shipped. To maintain cleanliness levels in the SNO Drift, a car wash is employed to clean the rail car prior to its entry into the clean area. Once SNO is to be decommissioned, the D_2O will be returned to the surface in the same way. After passing through a prefilter (FR05), the virgin D_2O is stored in a 60 tonne holding tank (TK03) which provides a constant supply to the remainder of the purification system. (All the filters found in the system are essentially $0.2 \mu m$ in pore size). The D_2O nitrogen cover gas system, which is separate from the light water one, is linked

with the purification system in order to maintain, in a closed loop, any evaporated D_2O from such things, among others, as rail cars and holding tanks. The D_2O is subsequently recovered from the cover gas system and returned to the purification system. Any columns attached to the purification system are also connected into the cover gas system so that when they are removed for assay, air doesn't come in contact with the contents (and D_2O vapors are not lost). Avoiding contact with mine air is essential to avoid contaminating the column prior to its assay.

Initial purification is achieved with the use of RO1 and RO2, which with its concentrate returned to its feed is defined as Loop 1, operating from TK03 only at a 195 litres per minute (lpm) feed flow rate. The permeate, flowing at 187 lpm, is directed to TK02 and the concentrate, at 7 lpm, can also flow to the Low Flow Ra Monitoring section. Three MnO_2 or ion exchange columns (AC04 to AC06) and an Ultrafiltration membrane (UFR03), constitute the Low Flow Ra Monitoring portion. The concentrate from UFR03 is first filtered and then returned to the RO1 feed. The permeate is directed to TK02. The columns can then be removed and counted by any one of the various emanation based counting systems.

The water can also be degassed and monitored from TK02 either in stand alone mode or simultaneously with the RO systems running. The water from TK02 first goes through¹ the degasser (DG01) from which the vapors are fed into the Radon Board for measurement in Lucas Cells. The 20 lpm water stream then flows through the mixer (MX02) back towards TK02. The overall reduction factor in Ra per pass for the degasser is expected to be five.

Once the system has been operated for a long enough period and purified a sufficient quantity of water, the initial fill may commence. A small flow is bled from the degasser and is directed into the chiller (HX02) to bring the water temperature down to the desired 10° C. Following the chiller, the water goes through UFR05, another Reverse Osmosis membrane, with the permeate to the AV and the filtered concentrate is directed to the tank VE01. The contents of VE01 can be emptied into TK02 periodically by operating RO1 in the purification mode from VE01. The

actual fill rate will be determined on site and will be less than the allowed maximum of only 20 lpm, which is the flow through the degasser, in order to maintain efficient degassing. The light and heavy water are to be added to the detector simultaneously although the fill rate for the heavy water must be less than that of the light water, and this must be done with an adequate margin for the light water system to be able to respond to a growing level differential. During the beginning of the fill and at the end (when filling the neck of the AV), the heavy water system must be limited to no more than 1.3 lpm otherwise the light water system will not be able to keep up and both water systems will automatically shut down. Once the AV and cavity are filled, RO1 can remain in operation and recirculate the heavy water in order to continuously purify it as impurities will always be leaching into the heavy water and building up if left unchecked.

Just as the virgin D_2O was transported down to the water system, the same railcars would serve to bring down the 6% brine solution for the salinated NC measurement modes. The brine is pumped through FR05 and into TK03 at 50 lpm, thus a 70 to 100 minute transfer time per railcar. The entry point would be flushed with one tonne of clean D_2O after all the brine has been transferred to TK03 in order to recuperate any brine residues. If necessary, the brine can be cleaned up at 20 lpm through an ultrafiltration unit (not shown in figure 3.4) prior to being mixed in with the D_2O from the AV. The brine is directed from TK03 into MX02 where it is mixed with clean unsalted D_2O , it then flows through HX02 and UFR05 before going back into the AV. The concentrate from UFR05 is returned to the feed for Loop 1. Since the heavy water must also be recirculated during salination, the unsalinated D_2O is taken from the permeate of RO1 at 187 lpm and added to the brine which is at 8 lpm. The time required to salinate the D_2O is expected to be on the order of three and a half to four days if the system is operated on a 24 hour basis.

Desalination is achieved through a two stage process: Desal 1 and 2. Initially, the D_2O is at a 0.25% salt concentration. By operating RO1 and RO2 with the

permeate from RO3 (Desal 1) either returning to the feed of RO1 and RO2 or to their permeate side, two effects can be achieved. The result of the RO3 permeate going back into the input of the first stage pair of ROs is a lower flow rate with a better quality permeate returning to the vessel. When the RO3 permeate is added to the first stage permeate, the flow rate for the procedure is increased but the salt concentration returning to the vessel is higher. The concentrate is accumulated in TK03 at a rate of 6 lpm which is made up in the AV from both TK02 and VE01. The time requirements for Desal 1 are identical to that of salination. Once the salt level in the concentrate falls below acceptable limits as the salt level in the AV becomes very low, Desal 2 can be implemented. In this instance the concentrate from RO3 serves as input for RO4 rather than being directed to the brine holding tank TK03. The concentrate from RO4 is then directed to TK03 for storage at 0.5 lpm. Considering the low concentrate flow from RO4, it is apparent that Desal 2 requires a longer operating time before the salt level in the AV falls below that which no longer gives rise to a detectable NC signal.

The high flow columns are designed to sample large volumes of the heavy water for radium. The permeate from the columns is first passed through UFR01 from which the permeate is filtered and returned to the AV. The concentrate from UFR01 is directed to VE01. The main purpose of UFR01 is to ensure that the fines from the columns do not make their way back to the AV. In such an instance, some of the activity that would normally remain in the column would return to the AV, and to make matters worse, the fines would continue to accumulate activity as they circulate around in the AV. If these fines were to settle out onto the AV surface, they would in essence become immobile sources and be very difficult to remove.

The alternate radium assay mode requires the use of RO1 through RO4 where the permeate from the last stage is returned to the AV through MX02, HX02, and UFR05. The concentrate flows through the assay columns AC04 to AC06 before making its way to UFR03. Permeate from UFR03 is returned to the AV through HX02 and UFR05. The concentrate from UFR05 is filtered and directed to the

RO1 feed. The concentrate from UFR03 is also filtered prior to its return to the RO1 feed. Again, the use of the ultrafiltration units stems from the fines produced by the columns.

The lead assay mode, which requires RO1, RO2, RO4, and RO5, serves as an independent measure of the Th level in the D₂O. The ROs would be run in a cascade mode with the concentrate from one stage feeding into the input of the next stage. The permeate from the RO units is directed back to the AV through MX02, HX02, and UFR05 (whose concentrate is returned to the RO feed). After running for several hours with the concentrate of RO5 in recirculation mode, the process can be terminated and the concentrate collected into a clean 500 cc bottle for subsequent analysis. The treatment of the operation of the RO and the subsequent chemistry steps, the elution and precipitation of the recovered lead carrier along with the very few ²¹²Pb atoms, involved in preparing an α source are the focus of chapter 4. Details pertaining to the efficiency of lead carrier recovery and blank levels measured for each step are given where possible, and the final forms of the RO, elution, and precipitation stages are presented along with details concerning their development.

In order for the entire system to be effective, the materials with which it is constructed must be of an acceptable purity such that the system does not contribute to the background level of SNO rather than reducing it. All components were chosen of high cleanliness polypropylene plastics with some necessary metallic parts (such as high pressure pumps) made of Hastelloy. Design choices were made by maximizing the effectiveness with a minimum of components such as valves. Valves in particular are undesirable from a radioactivity point of view since they generally contain a number of O-rings which are hot radon sources in terms of the levels of concern for SNO (even when lower activity substitutes were found).

Obviously, from the operation mode descriptions, it is apparent that the brunt of the purification is accomplished by reverse osmosis (which also salinates or desalinates the water). The remainder of the system is for assay and the associated preventive measures against fines from the columns. As mentioned earlier, the assay

columns will give rise to fines which must be prevented from making their way back to the AV. The UFR series Ultrafiltration units serve that purpose, and they are backed up by 0.2 μm filters as well. The reverse osmosis portion therefore removes a large fraction of the thorium in solution by retaining it on the retentate (or concentrate) side of the membrane, and forcing the water through to the permeate side. Despite the effectiveness of the RO and because of the large total surface area available, radon always manages to penetrate through the PVDF and into the water stream. When the radon, which has entered the system behind the RO, decays to lead. The process degasser was incorporated into the system to deal with this radon input. The processed water stored in TK02 can be degassed by DG01 and recirculated back to TK02.

The assay of lead, the topic of Chapter 4 below, along with the assay of radium and radon are thus the only means of determining what the thorium and uranium concentrations are in the heavy water. Since the neutrino signal background is determined by these concentrations, the assay techniques are very important indeed; that is why they are an integral part of the purification system.

Chapter 4

Lead Monitoring for The Heavy Water Purification System

4.1 The Need for The Assay of Th via ^{212}Pb

With an expected NC neutrino signal of merely 10 events per day in 1000 tonnes of heavy water, the need to limit the background to 10% of that, or 1 event per day per 1000 tonnes, is great if a clear signal is desired. Despite the effectiveness and adequate sensitivity the radium assay techniques may have, the thorium chain will nonetheless be out of equilibrium. Such disequilibrium may result from the influx of radon from the detector components and from the air surrounding the purification system itself. The only way to determine the level of disequilibrium would be to assay for one of the daughters after radon. Inspection of the decay schemes in figures 3.2 and 3.3 reveals that the best and only candidate for analysis in the thorium chain is ^{212}Pb , with a half-life of 10.64 hours. At the 3×10^{-15} g/g level for thorium and uranium, only 0.67 ^{212}Pb atoms are expected per tonne of heavy water if secular equilibrium is assumed. A sample size of 288 tonnes represents a mere 193 atoms of ^{212}Pb . Clearly, the most difficult task pertains to the assay of the supported and un-supported ^{212}Pb which is the focus of this thesis and in particular this chapter.

The best choice to assay is ^{212}Pb since all others after radium are of very short half-lives ranging between 60.60 minutes (^{212}Bi) and $0.3\ \mu\text{s}$ (^{212}Po) and would not survive the time required for the chemistry procedure assay. The daughters of ^{212}Pb of interest for α spectroscopy, namely ^{212}Bi and ^{212}Po , produce high energy α particles of which the highest is at 8.78 MeV from the decay of polonium (with a branching ratio of 64%). This α particle is actually of the highest energy of all the naturally occurring α particles. The background signal in an alpha spectrometer at that energy is therefore very small owing to the uniqueness of that particular α particle energy. Only emanation of ^{220}Rn from the materials surrounding the SSB can give rise to a background signal.

The heavy water purification system, reviewed in detail in section 3.5 of chapter 3, is the starting point for lead assay since access to the heavy water cannot be gained elsewhere. With an initial concentration of less than one atom of ^{212}Pb per 1000 l of water it is readily apparent that an initial preconcentration of the lead down to a much smaller and manageable volume is required in order to have any hopes of detecting the decay of the lead daughters. The reverse osmosis (RO) portion of the water purification system therefore serves the purpose of preconcentrating a large multitonne heavy water sample down to a few hundred millilitres. In doing so, the RO also accumulates in the downsized water sample a few hundred ^{212}Pb atoms (which were initially complexed with EDTA when in the AV to promote a more efficient separation.) The now manageable lead and water sample can be chemically treated to form a solid sample suitable for α -spectroscopy. There are two major steps involved in making a solid source and they are the separation of the lead from the complexing agent by elution with a cation exchange resin and the final precipitation of the released lead sample into a solid as PbCrO_4 . In order for the lead assay technique to be viable, the background contribution (or blank) from all the procedures and manipulations should not exceed at the very least the α signal expected from the few surviving ^{212}Pb atoms, hence the blank contributions from all possible sources must be measured such that they can be controlled and

reduced if necessary. The separation and recovery of the maximum possible amount of stable lead carrier and ^{212}Pb is also of paramount importance in order to obtain the strongest possible signal from the sample, thus the separation or recovery of lead must be determined for each major step of the technique as well. The details concerning all these aspects of the assay technique are therefore the focus of the remainder of this chapter.

With regards to neutral current detection in SNO for the case where tubular nickel proportional counters are deployed in the heavy water, the lead assay technique described in this thesis can be used, provided the lead doesn't plate out onto the nickel surfaces. On the other hand, should SNO use MgCl_2 (or NaCl) as an additive for NC enhancement, the assay of lead via preconcentration by reverse osmosis would be rendered inoperable because of the high osmotic pressure (about 800 psig) from the high salt concentrations achieved after the first stage of RO.

The normal sequence of chemistry procedures for testing the technique of ^{212}Pb assay requires that the ^{212}Pb spike be made beforehand then added and mixed into the one or two tonnes of UPW held in the 1 Tonne Test Facility tanks. Before anything else can be done, the spike must be recouperated by preconcentration via RO down to a manageable volume. Once the spike has been extracted from the tonne or so of UPW and is contained in a 500 cc bottle, more work must be performed on the concentrate before the lead can be precipitated. Due to the presence of EDTA which is necessary for efficient RO separation, the lead must be separated by cation exchange and subsequently eluted. The lead contained in the eluate from the elution stage can now be precipitated into a solid α source and counted in an α spectrometer. The sections pertaining to the above procedures aren't presented in the normal order of usage but rather in the order in which they were developed for clarity and continuity. We first begin with some introductory remarks followed by the alpha spectrometer development since it is essential the spectrometer be ready before any sources or blank measurements can be made. The next two sections involve how liquid ^{212}Pb sources were first manufactured and then precipitated into

a solid for α -counting. Once the procedures for making spikes and precipitating them were set, the testing of the elution stage began followed with the final stage of the assay technique, reverse osmosis.

The main focus of most published work on the determination of lead pertains to either stable lead, in quantities of concern for human health, or ^{210}Pb [64]. Some relevant work has nonetheless been carried out with ^{212}Pb [35]. In almost all cases, the procedures employed for sampling the lead are complicated, time consuming, and worst of all prone to high backgrounds. Considering the small amount of atoms available for the present work, a more suitable method was sought. The requirements were simple: the time needed to perform the technique should be significantly less than a single half-life of ^{212}Pb (10.64 hours), a minimum amount of labware should come in contact with the solution containing the lead, the labware and the reagents should be as clean as possible, and the procedures should be carried out in a clean dust-free environment. Most of the published techniques tended to employ either electrodeposition [34, 31, 39] or solvent extraction from some adsorber medium such as MnO_2 [60, 25]. Alternative source preparation methods such as precipitation were covered in references [39] and [60] but for parent radionuclei. The final technique was adopted from Don Wiles.

Once the individual stages of the technique had been developed adequately, an effort was made to reduce the background levels of each stage from the α spectrometer to all chemistry procedures.

To minimize the time and number of manipulations required, it was suggested (D. Wiles, personal communication) that the best approach would be to precipitate the lead as PbCrO_4 . Once the precipitation procedure was decided upon and further tests were done with the presence of EDTA to complex and stabilize the lead in solution, a second procedure was introduced to effectively separate the lead from the EDTA. The elimination of most of the EDTA was necessary because of its interference with precipitation and this was attempted by eluting the EDTA and lead separately using cation exchange column separation [37]. Tests were then

2 1 2
OF/DE

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1910a ANSI/ISO #2 EQUIVALENT

PRECISION™ RESOLUTION TARGETS

carried out with a two stage reverse osmosis system simulating conditions in SNO. All three stages in the lead assay procedure; precipitation, elution, and reverse osmosis, are presented and discussed in detail in the following pages. In the cases of precipitation and elution, the final procedure will first be given followed by the discussions pertaining to its development.

4.2 The Alpha Spectrometer

Once the ^{212}Pb has been preconcentrated by the RO and a dry countable source has been made, an appropriate counting system must be used to detect the α particles emitted by the ^{212}Pb daughters. Silicon Surface Barrier detectors (SSBs) are well suited for α spectrometry and have several advantages over gas filled proportional counters, thus they are useful for the lead assay technique developed here. The thickness of the active area of an SSB need not be more than 100 μm to be able to completely absorb all the energy of an 8.78 MeV α particle (actually, only 68 μm are needed). Due to advances and improvements in microchip manufacture, SSBs are inexpensive and have an effective 100% efficiency for absorbing an α particle that enters the active area. In essence, the SSB is a reverse biased (of only 50 to 100 Volts) PN diode which requires only an average of 3.6 eV to produce an electron-hole pair (as opposed to about 30 eV for gases), hence the greater energy resolution for separation of closely spaced peaks.

Some disadvantages of an SSB are the small active area, the protective surface coating, and the possibility of radiation damage. The very thin aluminum surface coating which protects the silicon, and permits its cleaning, also causes the alpha particle to lose a small fraction of its energy during entry. Radiation damage is not a problem for the ^{212}Pb assay in SNO, even when working with sources, because the count rate is much lower than the threshold for damage. The small active area is dealt with by the precipitation of equally small sources. A Monte Carlo analysis showed that about 25% coverage of 4π is obtained for an SSB and α source of

similar diameter (about 2.5 cm) separated by 0.2 cm. At such a close distance, the resolution of the spectrum suffers, but this is only secondary to any increases in detection efficiency. The low 25% coverage of a source will prove to be the lowest efficiency of the entire technique, thus the greatest increase in signal strength would be achieved by a drastic increase in detection efficiency at the spectrometer level.

The initial counting system consisted of a 576A dual Ortec α spectrometer coupled to a 2048 channel ADC via hand made attenuators, an OR gate, and a HP-IB to Camac interface for a 80386 PC computer. The multichannel spectrum analysis software employed was written inhouse in C code. The vacuum for the dual chambers was provided by a vacuum pump capable of attaining 100 milli Torr. After many problems were experienced and solved with the hardware, it was decided to go to a commercially available system in order to avoid any further problems in data loss. The new system, with Maestro software, eliminated the need for extra hardware, aside from the spectrometer.

Improvements were made to the vacuum system which consists of the two α counter chambers, copper tubing, and the vacuum pump. To prevent any airborne room dust from being sucked into the chambers, small (2.5 cm diameter) 0.1 μ m membrane filters were added to the pump vent port as well as the spectrometer vent port. This precaution was needed to maintain the background level in the counter to an effective minimum. Since the chamber walls are made of stainless steel, they are not expected to contribute much to the background. The only other sources of background would be other materials present in the chamber: materials such as the sample tray holder (polypropylene), planchet holder (aluminum), and the membrane on which the source is collected (polysulfone). The less material that is exposed to the SSBs or that is simply present in the chamber, the lower the background level is bound to be. Since the planchet holder and tray eventually become sources through contamination, it was decided that they should be eliminated entirely. Attempts to clean the polypropylene sample holders failed even when sonication in Radiacwash detergent 1:10 and 10% nitric acid baths were tried. The levels detected with a

cleaned planchet and tray were in agreement with the 13 to 27 counts seen before cleaning. Hence, to eliminate the sample tray and planchet, the membrane on which the source is collected is mounted directly onto the SSB (at a distance of about 0.21 cm from the detector) with a 0.1 cm thick polypropylene cap that fits onto the SSB. This effectively blocks out the rest of the chamber from the view of the SSB and reduces the background by a factor of four. The snug fit of the cap doesn't prevent a vacuum from forming near the SSB, but prevents alpha particles originating from elsewhere outside the cap from reaching the SSB. The diffusion rate of ^{222}Rn atoms through the plastic cap is calculated to be 2×10^{-5} atoms per day. The ^{220}Rn on the other hand doesn't live long enough to diffuse through the cap even at the level found for ^{222}Rn . Since only the energy region above 6.1 MeV is used, the background contribution from ^{222}Rn emanated from the inside cap surface can be ignored for the most part and we are left with the ^{220}Rn emanated on the inside of the cap contributing to the background.

Calibration of the geometric efficiency of both chambers was attempted with an ^{241}Am alpha source because the Monte Carlo technique could not differentiate between chambers. The ratio of the counts observed over a period of five minutes in chamber A (10487 ± 102) to chamber B (9400 ± 101) resulted in an 11% difference. Small differences in the position of the planchet from chamber to chamber are visible by eye, hence most of the 11% difference may be due to this. Since the planchet cannot be placed in an identical position from run to run, the 11% difference in geometric efficiency was not taken into account and is expected to cause a random uncertainty of lesser or comparable amount. The count rate observed divided by the activity of the americium source (2.56×10^4 decays per minute in 1995-06) times the five minute acquire time yields efficiencies of 8.2% and 7.3% for chamber A and B respectively. The difference between the apparent 7-8% geometric efficiency and the 25% predicted by Monte Carlo can be ascribed to the greater separation between source and detector and the fact that the source was also off center and irregular in shape. Simple geometric calculations assuming a point source give numbers eight

to fifteen percent points higher than the 25% from the Monte Carlo analysis. The difference in this case is due to the fact that the source was distributed for the Monte Carlo and not a point source.

A long term straight detector background result is shown in figure 4.1. An identical run made earlier showed an activity for chamber A (capped SSB) of about half that of chamber B (uncapped SSB), whereas in figure 4.1, the reverse is true. In chamber A, the SSB was covered with the plastic cap that came with it whereas in chamber B, the SSB was not covered, but the chamber walls were covered with two layers of Parafilm and the tray and acrylic planchet were present. For the region above 6.1 MeV, the first run detected (0.42 ± 0.19) cpd (capped) and (1.00 ± 0.29) cpd (uncapped). In the second run, the capped SSB detected (0.266 ± 0.098) cpd and the uncapped one (0.178 ± 0.072) cpd. The first background measurement lasted 287 hours and the one shown below was acquired over almost 811 hours. The system was never opened between runs. The differences in the spectra must therefore be due to the decay of contaminants present inside the chamber and from emanation from the SSBs, chamber walls, Parafilm, tray, and acrylic planchet. The rate for the capped SSB was slightly greater and this may be due to the greater proximity of the SSB to the cap, whereas in chamber B, the closest apparatus is the acrylic planchet which was a few millimeters further away from the SSB. At least, at these levels, variations aren't of any great consequence to the lead assay technique. Thus the blank from the spectrometer and the cap is (0.27 ± 0.16) cpd.

To obtain such a low detector background level, care had to be taken not to introduce any contaminants into the chamber or onto any surface therein. In the end, to avoid contaminating the chamber, latex gloves would be worn at all times when working inside the chamber. Any items removed from the chamber would be immediately wrapped in Kimwipes and cleaned with methanol before being reintroduced. Precipitated sources would be placed inside the cap and onto the SSB. The walls of the chamber would be wiped with methanol as a precaution and the chamber immediately closed and pumped down to 100 milliTorr. Preventing the

Figure 4.1: Long term background data for the dual chamber alpha spectrometer where the SSB in chamber A has been capped and the one in B has not and where the chamber also contained some Parafilm lining, a planchet holder, a tray. The system had been under vacuum for about six weeks and the data above was acquired during the last four weeks. The shift in the peak locations for the lower graph (corresponding to data acquired in chamber B of the spectrometer) is due to the use of the calibration data of the upper graph (acquired in chamber A).

buildup of dust in the chamber would then ensure the lowest possible background level, provided calibration sources and the like did not by chance contaminate the SSB or cap. Owing to its very thin nature, the SSB background from gamma rays would be virtually zero except for the chance occurrence of a ray traveling horizontally through the diameter. The only other possible contribution to the blank would be beta-alpha coincidences which add up to an energy greater than 6 MeV. At very low activities however, coincidences of that sort are not expected to be frequent at all: on the order of 6%. This effect is most evident on the trailing edge of the 8.78 MeV peaks in figures 4.5, 4.6, and 4.7 for example.

Even after 811 hours of continuous counting, no 7.7 MeV α 's from ^{214}Po in the ^{238}U chain were detected. This effect may be due to the very long half-life of ^{222}Rn of 3.8 days during which the radon has time to diffuse out of the chamber. In the event that such a background contribution should be detected, simply increasing the energy window minimum from 6.1 to 7.7 MeV would eliminate any possible confusion of a ^{238}U chain α 's with those of the ^{232}Th . Because of the thin nature of the ^{212}Pb sources, very few α particles loose enough energy to be counted below a 7.7 MeV threshold. In other words, raising the cutoff to eliminate ^{238}U background contributions (should they show up) would have little if no effect on the ^{212}Pb signal detected.

4.3 ^{212}Pb Calibration Sources and Spikes.

^{212}Pb was used for both the calibration sources and spikes needed to test the procedures. Because of the short 10.64 hour half-life of ^{212}Pb these were made only immediately prior to use. It was not possible to use ^{232}Th or ^{226}Ra sources because of the risks of contamination from these very long lived species. To avoid any chance of long term contamination, only ^{212}Pb sources and spikes were employed. In the event of mishaps, the lead contaminant would decay away naturally over a period of a few days.

A device was constructed which took advantage of the mobility of the ^{220}Rn daughter of ^{232}Th : a column containing 1.5 cc of MnO_2 spiked with a 100 Bq ^{232}Th source was mounted onto a retort stand and connected to a clean HDPE 1 l bottle. The bottle was fitted with a custom made lexan frit in the cap and a QuickConnect port. By attaching the bottle to the column and the column to a filtered compressed air source, it was possible to flow air across the MnO_2 , thus carrying the emanated radon with it, into the bottle containing a given amount of pure water. Even though the half-life of ^{220}Rn is only 55.6 seconds, the transit time from source to water was only a few seconds, hence the air radon mixture would bubble through the water where some of the radon would dissolve into the water. Once the radon decayed, it would be in solution as ^{212}Pb . Despite the great inefficiency of the apparatus, sources could still be made in the 10 to 20 Bq range. It was also possible to acidify or add $\text{Na}_4\text{-EDTA}$ to the water to ensure that once the lead was in solution it stayed in solution. 10 mg of EDTA or acidifying with HNO_3 to 0.2 M were applied to help prevent lead from plating out onto the bottle surfaces.

A test to determine the repeatability of manufacture of the prepared sources showed that the apparatus was capable of producing sources to within 10% of the expected activity. One of the main uses of these sources was for calibration of the α spectrometer. The 6.09 MeV (^{212}Bi) and 8.78 MeV (^{212}Po) peaks span the energy range of the spectrometer which was set to a range of 5 to 9 MeV. Sources made with the bubbler system were also employed in spike tests where the carrier lead recovery of a procedure could be compared to the radioactive species to determine if the stable lead could be used to track the radioactive lead. In those instances, the source would be split into two equal parts. The radioactive species recovery of a procedure would be determined by the ratio of the detected spectra between the half of the initial source which went through extra steps and the control half.

It was later realized that the bubbler system may have contaminated the One Tonne Test Facility and the reverse osmosis membranes. As air is blown through the thorium spiked MnO_2 coated beads, the violent agitation gives rise to MnO_2 fines

which are blown into the water reservoir. The thorium on the fines then becomes part of the ^{212}Pb spike and is carried over to the one tonne tanks as well. Some of the thorium which leaches from the MnO_2 plates out onto both the tank and membrane surfaces and becomes a source of contamination. On several occasions water was also accidentally introduced into the bubbler MnO_2 and blown back into the water reservoir. Since there were many spike tests carried out on the reverse osmosis system and one tonne tanks, the thorium contaminant level must have increased with use and subsequently given rise to detectable background levels.

4.4 Precipitation

Lead chromate is practically insoluble in cold water and it is insoluble in hot water, hence the ability to completely scavenge the lead from solution under favorable conditions. The solubility of PbCrO_4 in cold water, for example, is $5.8 \mu\text{g}$ per 100 cc of water [41]. Only traces of other elements are expected to be present in the solution during precipitation, even when the sample has been obtained by reverse osmosis, since the water is initially ultrapure (UPW). An Energy Dispersive X-ray Spectrometry (EDS) analysis as carried out on one of the precipitates (which had also seen the elution stage) showed some trace amounts of copper and zinc. The origin of these two elements may be an artifact from the EDS technique, otherwise their origin is unknown as neither element comes into contact with the solution. Their presence, on the other hand, doesn't interfere with the procedure. A small amount of stable lead must be added to the solution (about 0.1 mg) in order to have sufficient mass for the formation of crystals and to carry the few atoms of ^{212}Pb down with it. The final procedure is outlined in detail below where the chemicals and equipment required are also listed.

Chemicals required:

- 500 cc (or less) aliquot of UPW (Ionpure or Reverse Osmosis) or sample water.

- 60 cc of 1:3 NH_4OH (Seastar Ultrapure or equivalent).
- 10 cc of 1:50 NH_4OH (Seastar Ultrapure or equivalent), do not keep for more than a week.
- $\text{Pb}(\text{NO}_3)_2$ (BDH AnalR) for 1.000 mg/cc UPW Pb^{++} solution in either 0.4 M HNO_3 or with 100:1 EDTA:Pb.
- EDTA (Ethylene Diamine Tetra Acetic Acid) tetra-Na form (BDH assured).
- 2 cc of 1.5 M K_2CrO_4 (BDH AnalR).
- HNO_3 (Seastar Ultrapure or equivalent) for acidification of UPW to 0.4 M.
- 10 l of 10% nitric acid, reagent grade.

Molecular Weights:

lead nitrate: 331.20

lead chromate: 323.18

lead: 207.19

potassium chromate: 194.19

EDTA: 452.24

Equipment required:

- 1 l heatable PFA plastic beaker (Nalgene) with graphite base.
- Large flat PP lid.
- Aluminum foil.
- 1 l and 3 of 100 cc PP volumetric flasks.
- 25 cc PP buret.

- 100-1000 μ l micropipet.
- 1 cc disposable PP pipets.
- disposable micropipet tips.
- heating and stirring plate.
- Teflon stirring bar.
- Thermometer (glass).
- Plastic wall/glass tip pH probe (pH meter).
- 0.1 μ m pore size polysulfone membranes (Millipore VCWP02500).
- 200 cc plastic filter holder assembly (Gellman).
- PP erlenmeyer vacuum flask.
- Teflon rubber stopper for connection between flask and filter holder tap vacuum suction apparatus.
- IR lamp assembly.
- Plastic petri dish for filter containment.

Procedure:

Remove wristwatches and all jewelry from your hands and put on a pair of rubber gloves before any equipment in the fumehood is touched. A new pair of gloves must be used when placing the filter into the spectrometer. Line the fumehood with a plastic lined absorber which serves as absorber for spills, and change lining every few months. The filter holder components are kept in 10% nitric acid inside the large beaker at all times when not in use.

1. Empty the 10% nitric acid contents of the heatable beaker. Keep beaker covered. Remove the filter holder components one by one from the beaker and rinse them off with UPW before placing them face down in the fumehood to dry. Once all the holder parts are rinsed, carefully place a polysulfone filter onto the disk and assemble the holder components. Immediately cover the mouth of the holder with Parafilm and assemble with the PP flask; also connect the vacuum line to the tap and flask with a thick rubber vacuum hose.
2. Thoroughly rinse the heatable beaker with UPW and add a clean stirring bar along with 500 cc of freshly made water. Set the beaker down on a hot stirrer plate; cover the beaker with aluminum foil and puncture it in two places on opposing sides (cover holes with KimWipes when not in use). Acidify to 0.4 M HNO_3 first and then add 0.1 cc (equivalent to 0.1 mg of stable Pb^{2+} carrier) with a micropipet from the stock listed above. Turn on the stirring to about 60 rpm. When precipitation is preceded by elution add only 440 cc of water and the stirring bar because the carrier lead and acidity will be added with the eluate.
3. Fill the covered buret to capacity with 1:3 NH_4OH and position for titration over one of the punctures in the aluminum foil. Add the ammonium hydroxide slowly and dropwise. Calibrate the pH meter with dedicated standards (prepared under clean conditions with UPW water). Place the pH probe into the solution from the second puncture hole in the aluminum. The glass thermometer is also suspended in the solution at this point through its own hole in the aluminum foil. Add 1:3 NH_4OH dropwise from the buret until the pH reaches about 3.5 (remove buret and cover the hole in the foil) at which point a PP disposable 1 cc pipet is used to add 1:50 NH_4OH until the pH reaches 5.8. Dilute a few drops of the 1:50 NH_4OH in several drops of UPW and add to the beaker dropwise until the pH reads 5.90 ± 0.01 . Carefully rinse and

remove the pH probe and cover the hole in the foil.

4. Turn on the heating element of the hot plate (at a low setting) for about 10 minutes until the solution temperature rises to about 31° C, but when the temperature has reached 26° C, slowly add 2 cc of 1.5 M K_2CrO_4 dropwise first. Once the solution temperature has reached 31°, remove the beaker and set aside in the fumehood to cool for 15 minutes. Carefully rinse and remove the thermometer from the beaker and cover the hole. In our case the hot plate was calibrated and it was determined that setting number two permitted the heating of 500 cc of UPW to 30° C in ten minutes.
5. When the 15 minute cooling period has elapsed, pour 50 cc of solution into the filter holder reservoir (keep the reservoir covered with the piece of Parafilm that was originally placed on it after assembly). Use low suction only. Add more solution to the reservoir to top it off at 50 cc when the level drops below 25 cc. Continue until all the solution has been added. Measure 25 cc of UPW and add to the beaker to rinse out carefully and pour into the reservoir. The reservoir and the beaker are covered at all times except during transfers.
6. Once the solution and 25 cc of rinse water have all passed through the filter, turn off the tap water and disassemble the holder to remove the filter. Immediately and carefully place the filter into the bottom of a plastic petri dish and position it under the IR lamp for 15 minutes when open to air or at least 30 minutes when covered. Make sure the petri dish does not begin to melt underneath the IR lamp.
7. The dry filter is placed inside the alpha spectrometer by fitting the filter into the plastic cap of the SSB and placing it directly onto the SSB. Make sure the filter doesn't come into contact with the rim of the SSB. Count for 24 hours.

The original procedure (D. Wiles and I. de Jong, personal communications) involved a step to ensure the dissolution of lead oxides by boiling the solution

in 4 M HCl. This step was abandoned after tests showed that there wasn't any noticeable difference in the recovery. The acid concentration was also shown to be stronger than necessary and was subsequently reduced to 0.4 M (I. de Jong, personal communication). A prefiltering stage was also abandoned because nothing was ever caught on the prefilter. Hence, a substantial time saving was realized by eliminating these two steps, and this without effect on the stable lead recovery. To ensure a greater trapping probability of the precipitate crystals, the filter employed to extract the lead chromate was changed from a 0.45 to a 0.1 μm pore size. The use of a thicker bodied filter also eliminated losses from leakage in the filter holder. For the thinner filters, the two part filter holder assembly wouldn't clasp well enough to prevent leakage and we had to use a teflon o-ring. 2 mg of carrier were also added in the early procedure, and this proved to give rise to large self-absorption effects in the alpha spectra. An effective lower limit in carrier mass of 0.1 mg was suggested and this greatly reduced the alpha particle energy degradation evident in the spectra. The stable lead carrier recovery efficiency was initially determined gravimetrically but not when the stable lead mass used was only 0.1 mg (which is the limit of detection and uncertainty for the available analytical balances). Ultimately, the average time required to perform the precipitation procedure was reduced from the initial three and a half hours to a minimum of two hours and ten minutes. The least amount of time spent precipitating would allow sufficient time for the elution stage.

The optimal pH at which the precipitation was to take place was initially determined by testing the recovery over a pH range of 4.5 to 8. The behaviour of the test results in table 4.1 below are in agreement with what is expected [65, 14] for the chromate system where there is evidence of the formation of lead dichromate. The dichromate was formed as a result of the very high initial acidity of the solution. The FAA data proves that the lead content is as expected whereas the gravimetric lead carrier determination is erroneous. The titration curve (determined experimentally) of the precipitation procedure is shown in figure 4.2 below as

pH(± 0.02)	Pb Carrier Recovery % ($\pm 5\%$)	
	Gravimetric	FAA
4.52	117	-
5.05	131	-
5.43	139	95.0
5.99	151	98.5
6.51	179	99.0
7.02	125	-
7.50	184	94.0
8.01	117	-

Table 4.1: The stable lead carrier recovery (determined gravimetrically) as a function of the pH of the solution when the K_2CrO_4 was added to form the precipitate. The FAA data for some samples is shown for comparison.

well (titration usually requires 35 minutes because it is done dropwise). Accidentally greatly overshooting a pH of 6 would affect the carrier recovery (when determined gravimetrically) hence the need for a slow approach to the desired pH of 5.9.

Despite an obvious systematic error in the data which most likely is due to the formation of lead dichromate [65, 14] a general trend is visible. A hint of this trend also seems to be apparent in the FAA data but due to the close proximity of all the FAA numbers, it is more likely that the apparent trend is there only by chance. Above a pH of about 7 lead dichromate is not generally formed thus such a pH would seem preferable although lead chromate precipitation is best done at a pH of about 6. The choice of 5.90 was made on that basis and on the recommendation (D. Wiles) that it be below 6 as well. The solubility of lead chromate decreases with increasing temperature, thus the combination of a higher temperature than that obtained during titration and a pH of less than six renders lead chromate highly insoluble causing its precipitation.

A question as to the order of the titration and the addition of the potassium chromate was also investigated. Originally, the pH would be adjusted following the addition of K_2CrO_4 and it was found that the carrier recovery was lower at $(71 \pm 5)\%$.

Figure 4.2: pH curve for the precipitation procedure. As the pH increases more dilute solutions of NH_4OH are employed to avoid overshooting the desired pH of 5.90. The discontinuity in the curve near the pH of 3.5 is due to the reduction in the NH_4OH solution strength.

By adding the chromate ions after the pH adjustment, the precipitate would form under better conditions of acidity and the recovery was slightly higher ($86.5 \pm 5\%$). The results qualitatively agreed with investigations reported in references [38] and [42] where the order of addition of reagents was looked at. The specific surface of precipitates was found to be slightly greater when chromate was added to the lead. Optimal conditions for precipitation of lead chromate [42] were reported to be stirring at 60 rpm and aging afterwards for an hour. To avoid a lengthy procedure, the hour of aging was actually distributed between the 10 minutes of Step 4 (which generally begins with an initial temperature of about 25°C from the heat generated by titration), followed by a 15 minute cooling stage. The remainder of the hour is effectively comprised of the filtering stage which requires about 40 minutes. Strictly speaking, filtration of the precipitate was not intended for aging since once the solution has passed through the filter, aging is irrelevant. Only the portion of the solution remaining in the heatable beaker can be considered to be aging, hence portions of the solution age longer than others. The periodic agitation given to the solution when refilling the reservoir is also beneficial because the lead chromate crystals are known to dissolve and recrystallize rapidly to a greater degree with agitation. The recrystallization process does however slow down as the precipitate ages. With time, the dissolving and recrystallization of the lead chromate crystals acts on the ^{212}Pb which initially remained free in the solution and incorporates the ^{212}Pb into the crystals. This beneficial aging effect was reported by Kolthoff and Eggertsen [38].

There was some concern about the average size of the lead chromate crystals since, unlike many other precipitates, lower concentrations of lead and chromate were found to lead to smaller crystals [38] which may not trap as efficiently on the $0.1\ \mu\text{m}$ pore size polysulfone filters. Three Scanning Electron Microscope (SEM) pictures of typical precipitates of lead chromate crystals collected on one of the filters are shown in figure 4.3. The sufficiently great size and the distribution on the filter surface of the crystals is evident, and the cleanliness of the precipitate in general is

also apparent. In figure 4.3a, the dark grey shading is the filter showing through the precipitate. An X-ray diffraction analysis of a yellow precipitate (R. Conlon and G. Chao, personal communication) showed that the precipitate was definitely lead chromate in an orthorhombic crystalline structure and not lead dichromate, which can form under different pH conditions. The purity of the sample was evident from the X-ray diffraction spectrum as no unexpected diffraction peaks were found. The starfish and long needle forms of the crystals are welcome in that they offer a greater probability of being caught in between the fibers of the filter. No explanation can be given as to why there are two types of crystals and it is expected that the reason would have little effect on the results obtained. The precipitation of ^{212}Pb and stable lead (as carrier) as PbCrO_4 is therefore well suited for making thin sources of ^{212}Pb as evident in figure 4.3a. The thin depth of the precipitate is evident and implies near optimal conditions to minimize self-absorption from the source.

Due to the reagent requirements of the elution procedure discussed below, tests were also carried out to verify if any noticeable effects occurred when hydrogen chloride was replaced by nitric acid. Gravimetric analysis gave a 96.8% recovery for the nitric acid tests (which is also within statistical agreement with the HCl test).

Almost all of the precipitates were later on redissolved in a 10% nitric acid solution of known volume for analysis of the lead content by Flame Atomic Absorption (FAA). The membrane (containing the precipitate) in the 10% nitric acid would be placed on an orbital shaker (60 rpm) for a 24 hour period. The FAA lead carrier recovery results corroborated for the most part the gravimetric results. Evidence of dichromate formation was also seen in earlier precipitates, where the gravimetric recovery was found to be much greater than 100%, whereas the FAA results of the same precipitates were for the most part within the $100 \pm 5\%$ limit. The carrier recovery numbers for both gravimetric and FAA methods in table 4.2 represent the data subset where the precipitation procedure was employed under its near enough to or final form.

For those tests in table 4.2 which have both gravimetric and FAA recoveries,

Figure 4.3: a: 5,000x magnification of the surface of the lead chromate precipitate found on a 0.1 micron pore size filter. Notice the evenness of the distribution of the crystals. b: A much closer view of the crystals at 20,000x magnification where the crystal structure is more evident. c: A close up view of a cluster of lead chromate crystals at a magnification of 2,700.

Test	Grav.	FAA	Test	Grav.	FAA
T3A4	92.9	102	T5B1	92.7	112
T3B4	102	94.6	T6A2	95.9	-
T3A5	98.0	101	T8A1	99.3	100
T3B5	106	108	T8A2	-	97.5
T3A6	99.3	-	T8B2	-	105
T3B6	96.1	95.3	T8A3	-	95.0
T3A7	102	91.2	T8B3	-	92.1
T3B7	92.7	97.3	E1A3	-	94.3
T3A8	95.9	-	E1A4	-	95.7
T5A1	92.7	113			

Table 4.2: Gravimetric and FAA stable lead carrier recovery results for all successful precipitation procedures which were not carried out in conjunction with other procedures such as elution or the RO. The tests from T8A2 on could not yield gravimetric recoveries due to the 0.1 mg carrier mass being at the level of sensitivity of the analytical balance.

the average gravimetric recovery efficiency was determined to be $97.5 \pm 4.9\%$ which compares well to the corresponding average FAA recovery of $101.4 \pm 7.4\%$. Both numbers are in agreement to one standard deviation and all standard deviations quoted are mean value. For the full data sets the final recoveries are $97.4 \pm 4.1\%$ for gravimetric and $99.6 \pm 6.5\%$ for FAA which when combined yields a final number of $98.0 \pm 3.5\%$. The inherent uncertainty from the labware employed is calculated to be 4.5% alone. A higher uncertainty for the FAA data is a result of the variability brought in by the dissolving of the precipitates. Uncertainties associated with the gravimetric determination of the volume and with the measured density of the 10% nitric acid solution used for dissolving the lead chromate also contribute to the 6.5% FAA uncertainty above the usual uncertainties associated with the labware employed. The FAA process itself is uncertain, for the case of repeating the same measurement, by 0.6% at the high 12 ppm end and by 0.8% at zero ppm as determined from the variations in the standard solution calibrations that are carried out

periodically during a session. Of interest as well, and which is not shown in table 4.2, is that when the recovery falls (for any reason) below about 10 to 15 percent, the stable lead recovery cannot adequately compensate for any discrepancy in α spectra intensity between two samples of equal initial activity.

The precipitation procedure is therefore more than adequate from an efficiency point of view (with an efficiency of $98.0 \pm 3.5\%$) in recovering most of the lead (added in known amounts) from solution. The question remains as to the lowest radioactive background levels that can be expected from it. A considerable amount of effort was focused on this aspect of the procedure because the crux of the technique depends on a low enough background to enable the detection of the rare ^{212}Pb daughters in SNO UPW.

Controlling the low level procedural background, or blank, is the most difficult and demanding aspect of ultra-low radio-trace analysis. Of utmost importance, even above the actual blank level itself, is the reduction or limiting of the variability in the blank. An acceptably low blank with a high variability will greatly limit the sensitivity of any technique despite the low enough blank! [49] Most trace analysis work is performed at the sub ng/g level whereas SNO ^{212}Pb radioanalysis expects to be at a level of about 2.4×10^{-19} ng/g, or 670 ^{212}Pb atoms per 1000 tonnes of water. Some relatively recent work [44] on bioassay using α spectroscopy at the sub mBq activity range (one order of magnitude greater than that detectable by the α spectrometer) was carried out, albeit for a much more restricted energy window of 0.19 MeV in the spectrometer, which is an order of magnitude smaller than the 3 MeV window employed here. The authors also used electroplating for source preparation and had an equivalent background level 40 times larger than the (0.27 ± 0.16) cpd achieved by the author. An understanding of the origin of the sources contributing to the blank is important and essential if the blank is to be reduced and controlled [48, 13, 6, 69]. There are four origins of sources to the blank, namely from the environment, reagents, labware, and from the analyst, each of which is discussed in detail below.

The background battle begins with the environment where the low level work is to be carried out. The use of a laminar flow fumehood is essential to eliminate as much airborne dust as possible from the work area because dust also contains thorium and uranium (typically at the μg level per gram of dust) as well as the lead which is to be assayed. Despite the use of such a fumehood, dust particles may still be easily incorporated into the precipitates even though all open labware may be kept covered when not in immediate use. Laminar flow fumehoods contain High Efficiency Particulate Air (HEPA) filters to remove dust particles of about $0.3\ \mu\text{m}$ or larger (to a Class 100 specification); they remain the best possible method of dust collection to this day. Attempts to reduce the low level background for the ^{212}Pb procedure revealed that despite the effectiveness of the fumehood's dust removal, the thorium and uranium contained in the trapped dust eventually decayed to radon which would promptly emanate and be carried into the work area by the large air flow in the hood. Once the radon decayed to ^{212}Pb or ^{210}Pb it would become a contributing factor in the blank and would settle on all the equipment. This was shown to be the case simply by placing uncovered filters inside the fumehood work area. Alpha counting of several different filters, which were exposed in sequence for 24 hour periods or longer, gave rise to rather nice spectra of between 20 to 200 counts between 5 MeV and 9 MeV in a 24 hour counting period (figure 4.4). It is possible that despite the precautions where everything is kept capped or covered when not in immediate use, some dust particles (too small for the HEPA filters) and ^{212}Pb atoms do make their way into the solutions. The drying stage is also greatly susceptible to airborne dust and ^{212}Pb atoms. Reductions to the background can be made by drying the precipitate under an IR lamp as before, but inside a glass petri dish (placing the filter on some backing material to avoid contact with the glass surface) with a flow of inert gas. Added drying speed can be achieved with the above operation being done on a hot plate. The removal of gases, radon in particular for our purposes, from air flows is possible by use of absorbants and scrubbers but remains an expensive solution. The airborne radioactive lead problem

Figure 4.4: Example of airborne ^{212}Pb activity in fumehood. The lead originates from radon gas emanating from the trapped dust in the fumehood filters. The filter was exposed to the air in the fumehood for a period of 24 hours before being counted. The peaks correspond to ^{212}Bi (at 6.09 MeV) and ^{212}Po (at 8.78 MeV) decays in the ^{232}Th chain.

in fumehoods must therefore be lived with or circumvented by other means as the solution to the problem was not found in this thesis.

The negative air pressure in the room where the hood was built, a necessity due to the radioactive nature of the investigations, also poses a problem. Dust from outside the room would therefore be swept in underneath the door. The lack of HEPA filters for the room air system would leave the brunt of dust removal to the fumehood and wouldn't filter out the dust sucked in from underneath the door. All these uncontrolled dust sources would have an effect on the variability and ultimate level of the blank.

The reagents themselves may be sources of contamination for the blank since

they may also contain high enough levels of thorium or uranium to support the bothersome lead. The use of commercially available ultrapure reagents with lead contaminant levels in the 0.005 ± 0.005 parts per billion (ppb) effectively eliminate them as sources of background as this would only give rise to some 0.01 counts per day in the spectrometer for the aliquot of acid required, and this in part is also due to the small amounts of reagents required. Despite the plastic bottle and wrap that is used to contain the reagents, radon atoms can and do diffuse through the container walls at a rate of about 8 atoms per day for ^{222}Rn [70] (as does the acid in the reverse direction). Once equilibrium has been reached after about 5 days (mean life of ^{222}Rn), the radon level in a given 250 cc bottle of reagent is about 40 atoms which thankfully is insufficient to be noticeable in any spectrum acquired in a 24 hour period because of the 22 year half-life of ^{210}Pb . Although ^{220}Rn cannot penetrate the plastic barrier in its lifetime of less than one minute, when the bottle is opened, airborne dust (which gives rise to ^{220}Rn) and atoms are absorbed into the solution and reagents and may contribute in some small way to the blank. Any daily variations in atmospheric pressure and humidity will affect the levels of radon in room air which in turn will affect the levels dissolved into reagents and solutions. These fluctuations are expected to contribute to the variability of the blank in much the same way as the fumehood undoubtedly does.

This brings us to the question of the labware. High bulk purity plastics are the rule for ultratrace analysis work since contaminants in the bulk of the material can leach out from near the surface or eventually give rise to radon which emanates into the contents. Materials such as TetraFluoroEthylene (TFE), Teflon PerFluoroAlkoxy (PFA), or PolyVinylidene Fluoride (PVDF) are essential. They must also be initially rigorously cleaned and their history must be known to prevent contamination from unexpected sources. A 10% nitric acid bath for extended periods is sufficient to accelerate the leaching of the contaminants near the container surfaces thereby reducing its effect on the blank. This is why all labware which comes in direct contact with the solution to assay, such as the heatable beaker and the

membrane holder, is always kept in 10% nitric acid when not in use. Use of much stronger acids is not recommended for this activates plastic surfaces which then act as ion exchangers thus removing atoms, such as lead in our case, from solution. Hydrochloric acid was replaced with nitric acid since there is the possibility that it may be difficult to adequately remove from surfaces after contact [6, 51]. Despite all the cleaning of surfaces, radon emanation from deeper within the material will still occur, hence the necessity to use the cleanest materials possible and to perform the assay in the shortest time possible. Wearing latex gloves is also necessary, not only from a safety point of view, but also to avoid depositing the oils from the skin onto the labware surfaces. The oils secreted by the human skin contain certain levels of thorium, uranium, and lead (at the sub ng level) which can conceivably contribute to the blank. Jewelry and watches are not to be worn in proximity of the solution when assaying to preclude any possibility of contamination. Finally, the use of rubber stoppers and rubber in general near the solution is to be avoided since they are relatively hot sources [13]; the use of Teflon stoppers is preferred. Another essential piece of apparatus that could be replaced is the aluminum surface hot plate and the aluminum foil covering on the heatable beaker. It would be preferable to use a ceramic hot plate in order to avoid having metal inside the fumehood near the solution. A plastic film could replace the aluminum foil as well.

Studies [56] have also revealed that, while in solution, dissolved ions can plate-out onto metallic and plastic surfaces alike. This would in effect rob the solution of a fraction of its ionic lead atoms (20% when in UPW only) unless measures are taken to prevent this occurrence. To avoid lead plate-out as much as possible, ^{212}Pb spikes or stable carrier should not be kept in a solution without either 0.2 M HNO_3 or 100:1 EDTA:Pb present. The acid or the EDTA should be added to the UPW prior to the lead. The addition of 100 ppb EDTA in the plate-out study has shown that a reduction of three to seven times of the expected plate-out occurs. Despite these precautions, there remains a small plate-out effect which can invariably contribute to the systematic error. Even the stock solutions which contain lead and EDTA or

nitric acid are prone to some plate-out, hence the 0.1 mg stable lead in a carrier aliquot is most likely lower than expected by at least a few percent. This leads to a systematic error in the stable lead carrier recovery which is on the low side. To avoid this systematic error, an aliquot of the feed should also be analysed along with the samples and the results corrected for the feed stable lead content.

Variations in the concentration of stock solutions from evaporation over long times also can lead to systematic errors in the calculated recovery efficiency. Plastic labware [48] are not airtight as one might assume. Some containers, such as those used for the ultraclean acids, even support a small amount of acid diffusion through the container walls. The effect can be minimized by using concentrated stock solutions for which small variations in the nominal concentration are acceptable and by independently measuring the feed used as a spike.

In essence, excesses and purity of reagents, time, labware cleanliness, and the analysts technique all influence the blank and give rise to its variability over time as these conditions change. The full procedural blank data for the precipitation procedure can attest to this as evident in table 4.3 where the results for several blank runs are presented.

Because the number of counts are generally quite low, it is dangerous to make inferences from the data and this also leads to the 6.09/8.78 peak ratios being off somewhat. Previous blank analyses with HCl, the uppermost set of data in table 4.3, have shown that the blank is highly influenced by the reagents employed. In the first instance, only regular Analab grade reagents were used which were stored in glass bottles. Progressively, the reagents were changed over to the ultraclean variety one by one. The benefits are clear for the case of HCl, but on the other hand, for tests involving nitric acid (all the T8 series tests), the differences are not readily apparent. A simple comparison of the two data sets reveals that for the region above 6.1 Mev, both averages are 3.2 ± 3.0 cpd. It should be noted that the precipitation procedure had undergone considerable changes between the time the blank tests with HCl and HNO₃ were carried out. The use of ultrapure reagents

Run #	Corrected Spectra		
	Total	<6.1 MeV	>6.1 MeV
0Ur	90	28	62
1Ur	52	22	29
2Ur	15	4	11
3Ur	5	1	4
T8A1	13	6	7
T8A2	3	3	0
T8B2	10	6	4
T8A3	7	5	2
T8B3	0	0	0
T8A4	12	4	8
T8B4	6	3	3
T8A5	6	1	5
T8B5	4	2	2
T8A6	1	0	1

Table 4.3: Alpha spectrometer data for several blank runs for the two α peaks (regions of interest) from ^{212}Pb daughters. The first four T8 tests were with AnalR reagents and the subsequent tests were carried out with ultrapure reagents under identical conditions. All results are for precipitation only and include the straight detector background. They have also been corrected for the stable lead carrier recovery determined by FAA. The first data set shown was carried out earlier to demonstrate the necessity of ultrapure reagents (no recovery correction by FAA). The run number designates how many reagents were ultraclean in that particular trial. The <6.1 MeV column represents the 6.09 MeV ^{212}Bi α decay (BR=36%) and the >6.1 MeV column the 8.78 MeV ^{212}Po α decay (BR=64%). The xUr notation stands for X number of Ultraclean reagents employed.

remained part of the procedure despite the above data since AnalaR grade reagents cannot be trusted or guaranteed to be clean at all times as the ultraclean reagents are. Nevertheless, the data also remains valid as the contribution to the blank for the precipitation procedure (coupled with the counter background, of course).

4.5 Elution

In this next step, involving the separation of lead and EDTA, the EDTA must be separated reasonably well to permit the efficient precipitation of the said lead carrier. The great stability of the lead-EDTA complex, which is most desirable when in the acrylic vessel and the reverse osmosis system, becomes rather bothersome when the lead must be precipitated into an alpha-countable source. The procedure outlined in this section concerns the extraction of the lead from the Pb-EDTA complex by adsorption onto an appropriate ion exchange resin. The elimination of the now undesirable EDTA is the first step in the elution process which is then followed by the elution of the lead carrier itself together with the few tens of radioactive ^{212}Pb atoms. The actual procedure, modified in part by Cathy Shewchuk and Michal Shatkay, is modelled after a method described by Khopar and De [37]. The final procedure is given below before the details are discussed as to the reasoning behind the steps and the modifications which were made.

Chemicals Required:

- 300 cc UPW (Millipore 18.2 M Ω cm or equivalent).
- 100 cc 4 M HNO_3 (Seastar Ultrapure or equivalent).
- 10 cc Dowex 50W-X8 Hydrogen form Cation Exchange Resin (50-100 mesh).

Equipment Required:

- 30 cc Teflon beaker.

- 2 cc (10 cc reservoir) Poly-Prep Chromatography Column.

Procedure:

All work for the elution procedure, as with precipitation, should be carried out inside the clean fumehood work area and with similar caution and attention to the blank. Latex gloves are to be worn at all times.

1. Measure out with a plastic spoon about 10 cc's or so of Dowex 50-X8 resin and place it inside the teflon beaker. Cover the beaker with parafilm immediately. Prepare the resin for use by immersing and rinsing it ten times with 4 M HNO_3 acid followed by ten rinsings with UPW (keep beaker covered when not pouring reagents into it). Keep the resin under cover of water at all times. Prepare the PP column by adding a few cc of Acetone. This will wet the plastic porous bed support disk and facilitate the flow of water through it later on. Keep the cap on the column whenever it is not being refilled. All eluates with the exception of the one for lead is to be collected in a waste container.
2. Carefully add the 50W-X8 resin into the PP column while gently tapping the sides to aid in the settling of the resin and to avoid the formation of bubbles. Do not let the resin go dry; always keep well covered with solution or water. Once the settled resin reaches the 2 cc mark, the column is then full and ready for the secondary pretreatment. Add 10 bed volumes (20 cc) of 4 M HNO_3 acid to the resin in two 10 cc aliquots. Before the acid level falls below the resin bed surface, add UPW to the reservoir. Periodically check the pH of the eluate with litmus paper and continue adding UPW until the pH has risen to 6. The column is now ready for the lead-ETA spike.
3. At this point in the procedure there are two possible avenues to pursue depending on the origin of the spike. If the spike is the concentrate from the reverse osmosis system, it will be in a 500 cc PP bottle fitted with a spigot and

Tygon tubing at the bottom. By attaching the tube to a hole in a specially made column cap, the concentrate can be transferred from the bottle to the column. The flow must be regulated with a constriction valve on the outside of the tubing to no more than 1 bed volume per minute (BVM). The other option refers to instances where spikes were made on the bubbling system. To avoid unnecessary transfers, the spike is added directly to the column in aliquots from the bottle in which the spike was originally made. Do not let the spike level fall below the resin surface. At this point, the lead has been adsorbed onto the resin as well as most of the EDTA.

4. Once the spike has all been passed through the column, add 260 cc of UPW to rinse off most of the EDTA. For the RO spike case, add the water to the bottle and regulate the flow as before. The final step before elution of the lead requires the addition of 36 cc of 0.015 M HNO_3 as insurance that all the EDTA that can be has been removed.
5. Now that most of the EDTA has been removed, the lead can be eluted from the resin with 60 cc of 4 M HNO_3 . Collect the eluate in the heatable beaker which has been emptied, cleaned, and covered with aluminum foil according to the first steps of the precipitation procedure. Add only 440 cc of UPW instead of 500 prior to the lead elution. The 4 M HNO_3 acid is therefore diluted to 0.5 M. The precipitation procedure may be carried out from this point.

The original elution procedure tests were carried out with 5:1 EDTA:Pb spikes which helped determine what volumes were adequate for the various elution steps. Many small consecutive aliquots were taken for each eluant and later analysed by FAA for lead content. A trial elution run, at the 5:1 EDTA:Pb level, was performed by Cathy Shewchuk and the author to determine the effectiveness of the UPW wash for removing the EDTA from the resin and column. The EDTA content of

Sample Description	Volume ml	EDTA mg
Feed(5mg EDTA)	10	4.88
Feed eluate	12	0.36
UPW wash #1	12	1.76
UPW wash #2	12	1.68
UPW wash #3	12	0.74
UPW wash #4	12	0.12
UPW wash #5	12	0.00
0.015 M HNO ₃ (x3)	36	0.00
4 M HNO ₃ (x4)	32	0.00
Total EDTA eluted	140	4.66

Table 4.4: Amount of EDTA eluted per aliquot of eluant for a 5:1 EDTA:Pb spike containing 5 mg of EDTA. Note that after the fourth UPW wash the amount of EDTA eluted was below the detection limit the the technique despite the use of progressively stronger acidic eluants. The sensitivity of the EDTA determination was less than or equal to 0.04 mg of EDTA.

the aliquots was subsequently measured by Michal Shatkay and the results of the analysis are shown in table 4.4.

All of 95.5% of the EDTA was effectively removed by the first 60 cc of eluant of which one fifth of the volume was simply the eluate from the feed which contained 7.4% of the EDTA that didn't adhere to the column in the first place. The results were at first encouraging, hence it was decided that the lead content for another trial elution run, 5:1 EDTA:Pb, be measured so that the carrier recovery could be known as well. Table 4.5 contains the data for the stable lead carrier elution and FAA analysis.

In order to be more than reasonably sure that most of the lead would be eluted, the 4 M nitric acid elution step was employed as the full 60 cc's indicated in table 4.5 despite the low gain in recovery per step, since the short twenty minute time

Test EDTA:Pb	Calculated Pb Spike	FAA of Spike	FAA of ppte or eluate	FAA of filtrate	Ppte/ Spike	Eluate/ Spike
	(mg)	(mg)	(mg)	(mg)	%	%
5:1	1.002	1.055	1.019	0.000	-	96.6
5:1	1.002	1.152	1.256	0.000	109	-
100:1	0.2008	0.2025	0.2086	-	-	103
100:1	0.2008	0.2175	0.2096	-	-	96.4

Table 4.6: Stable lead recovery by FAA analysis for the elution procedure for 5:1 and 100:1 EDTA:Pb mass ratios. For the second 5:1 test listed, the eluate was precipitated, dissolved, and tested along with its filtrate. An FAA analysis on the eluate was conducted for the first 5:1 test and the two 100:1 trials hence precipitation was not possible. The two final columns, Ppte/Spike and Eluate/Spike, refer to the ratio of the FAA of Precipitate or Eluate over the FAA of Spike columns respectively.

period required for this was minimal enough. The small quantity of lead which was eluted during the initial UPW washes and the weak (0.015 M) nitric acid wash most likely came off complexed with the EDTA. The EDTA in that case may not have allowed the lead to separate to the cation exchange resin in the first place. A trial with lead carrier only, no EDTA, concluded that 3.4% of the initial lead spike remained on the column after elution. This is in reasonably good agreement with the data of table 4.5 where 8.6% of the lead was not recovered at the end of the elution where EDTA was employed. The 96.4% listed was first corrected by dividing by 1.055 to compensate for the 105.5% lead content of the spike, yielding a recovery of 91.4% (and thus a loss of 8.6%). The procedure was then tested for a EDTA:Pb concentration of 100:1 for which the data is listed in table 4.6.

Despite the variability in the data of table 4.6, it was assumed that there were no problems with the stable lead recovery. The variations were within the calculated and expected 4.5% uncertainty of the technique. Three blank runs were then carried out with ultrapure reagents; the results of these runs are listed in table 4.7 and designated as "UEP". When the precipitates were subsequently dissolved, it was

Test EDTA:Pb	Calculated Pb Spike	FAA of Spike	FAA of ppte or eluate	FAA of filtrate	Ppte/ Spike	Eluate/ Spike
	(mg)	(mg)	(mg)	(mg)	%	%
5:1	1.002	1.055	1.019	0.000	-	96.6
5:1	1.002	1.152	1.256	0.000	109	-
100:1	0.2008	0.2025	0.2086	-	-	103
100:1	0.2008	0.2175	0.2096	-	-	96.4

Table 4.6: Stable lead recovery by FAA analysis for the elution procedure for 5:1 and 100:1 EDTA:Pb mass ratios. For the second 5:1 test listed, the eluate was precipitated, dissolved, and tested along with its filtrate. An FAA analysis on the eluate was conducted for the first 5:1 test and the two 100:1 trials hence precipitation was not possible. The two final columns, Ppte/Spike and Eluate/Spike, refer to the ratio of the FAA of Precipitate or Eluate over the FAA of Spike columns respectively.

period required for this was minimal enough. The small quantity of lead which was eluted during the initial UPW washes and the weak (0.015 M) nitric acid wash most likely came off complexed with the EDTA. The EDTA in that case may not have allowed the lead to separate to the cation exchange resin in the first place. A trial with lead carrier only, no EDTA, concluded that 3.4% of the initial lead spike remained on the column after elution. This is in reasonably good agreement with the data of table 4.5 where 8.6% of the lead was not recovered at the end of the elution where EDTA was employed. The 96.4% listed was first corrected by dividing by 1.055 to compensate for the 105.5% lead content of the spike, yielding a recovery of 91.4% (and thus a loss of 8.6%). The procedure was then tested for a EDTA:Pb concentration of 100:1 for which the data is listed in table 4.6.

Despite the variability in the data of table 4.6, it was assumed that there were no problems with the stable lead recovery. The variations were within the calculated and expected 4.5% uncertainty of the technique. Three blank runs were then carried out with ultrapure reagents; the results of these runs are listed in table 4.7 and designated as "UEP". When the precipitates were subsequently dissolved, it was

apparent that more work needed to be done on the elution procedure to effectively remove the destructive effect the remaining EDTA had on the precipitation stage. The data for these new EDTA removal trials is also listed in table 4.7 where the change in the procedure consisted in increasing the UPW wash step from 60 cc to 260 cc. To save time, both the stable lead recovery and blank tests were combined into one by simply executing the procedure under optimal blank conditions, counting the blank, and then dissolving the precipitates for FAA analysis of the lead recovery afterwards.

The lead recovery for the T8 tests in table 4.7 was found to be unacceptably low and an excess of EDTA during precipitation was suspected as being the cause. There were two alternative classes of solutions to the excess EDTA problem: trying to remove more of the EDTA, or destroying the EDTA completely. The simplest solution consisted in trying to remove more of the EDTA by either increasing the amount of UPW employed in the rinsing stage or by trying to use a stronger eluant than UPW. Results for a 0.015 M nitric acid eluant were negative in terms of effect because the EDTA eluted by the weak acid was below the detection limit of the EDTA assay method. The UPW, considering how much EDTA it initially removed, was a better choice since with a weak acid, or especially a stronger one, some of the lead might be eluted early and lost. Regardless of the actual eluant (HCl or HNO_3) used, the added time required for the elution of EDTA with an increased volume of eluant would have been the same.

The second and more drastic option involved oxydizing the EDTA [54, 32]. Oxydizing the EDTA involves in the first step evaporating away the solution which is acidified with nitric acid. The methods referenced are well suited for the procedures developed in this thesis because they employ nitric acid in the first step. Further additions of nitric acid followed by evaporation constitute the second step. If unsuccessful in oxydizing all the EDTA at this point, small amounts of hydrogen peroxide can be added along with the nitric acid before evaporation. The added complications concerning contamination of the blank and the greater time required

to complete the oxidation make this option the less desirable of the two, hence the decision to try the increased volume of UPW as EDTA eluant.

With a total volume of 260 cc, the elution of EDTA by UPW is shown to be acceptably high as to permit reasonably high lead recoveries. Initially, the volume of UPW employed was 60 cc to which an additional 200 cc were arbitrarily added to constitute the new volume. Table 4.7 contains stable lead recovery data for a combined elution and precipitation procedure for an elution procedure employing only 60 cc (T8 series of tests) of UPW and for others at 260 cc. By comparing the recoveries it is readily apparent that the added UPW eluant has the desired effect.

The stable lead recoveries listed in table 4.7 have been corrected for the FAA numbers obtained on samples of the stock from which the spikes for the tests were taken. The lead in 0.2 M nitric acid solution stock for precipitation only was found to have $(97.2 \pm 4.5)\%$ of the stable lead expected and the 100:1 EDTA:Pb stock $(97.5 \pm 6.7)\%$.

The recovery is, on the other hand, not as stable as desired and is consistently lower, especially for the three last NB tests, even though the same procedure manages to provide recoveries in the seventy percent range for the ^{212}Pb El source tests. This is further evidence that EDTA interference with precipitation persists despite the increased UPW wash. Despite the interference from EDTA, the blank does not seem to be adversely affected. The corrected spectra above 6.1 MeV for all the blank tests, irrespective of recovery, are within the ten to thirty counts per day range with the exception of two high rates of seventy or ninety. This again is a manifestation of the variability and unpredictability of the blank. The average blank is therefore 20 ± 8 cpd in the energy window above 6.1 MeV to 9 MeV. If the the two higher count rates are included, the average increases to a staggering 34 ± 27 cpd. Blank rates as high as this will make detecting the ^{212}Po signal of about twelve counts uncertain. Of concern as well will be the contribution to the blank from the operation of the reverse osmosis stage of the technique which can only add to the problem.

Test Description	Recovery Pb (%)	Total cpd	<6.1 cpd	>6.1 cpd	Corrected Total	<6.1 cpd	>6.1 cpd
T8B6 UEP	11.5	3	0	3	26	9	17
T8A7 UEP	7.6	9	4	5	118	53	65
T8B7 UEP	7.2	3	3	0	42	15	27
NB1 E2P	68.2	17	9	8	25	13	12
NB2 E2P	88.1	33	14	19	37	16	21
NB3 E2P	43.6	22	8	14	50	18	32
NB4 E2P	56.5	11	4	7	19	7	12
NB5 E2P	53.6	52	6	46	97	11	86
E1A4 P	98.4	31017	10934	20083	3.1×10^4	1.1×10^4	2.0×10^4
E1B4 E2P	79.3	25979	9223	16756	3.3×10^4	1.2×10^4	2.1×10^4
E1A5 P	77.0	32790	11662	21128	4.2×10^4	1.5×10^4	2.7×10^4
E1B5 E2P	75.5	31644	11321	20323	4.2×10^4	1.5×10^4	2.7×10^4
E1A6 P	79.7	19890	7048	12842	2.5×10^4	8.8×10^3	1.6×10^4
E1B6 E2P	74.4	18068	6329	11739	2.4×10^4	8.5×10^3	1.6×10^4

Table 4.7: Stable lead recovery, full procedural blank, and ^{212}Pb source tests of the elution and precipitation procedures combined. The E1 series trials were all carried out with strong ^{212}Pb sources from the bubbler system. Both the T8 and NB series tests were carried out with ultraclean reagents and with the proper conditions for blanks. Please note that some spectra were appropriately corrected for missing counts in either half of the spectrum where counts originally didn't register. The <6.1 MeV column represents the 6.09 MeV ^{212}Bi α decay (BR=36%) and the >6.1 MeV column the 8.78 MeV ^{212}Po α decay (BR=64%). The units cpd are counts per day.

The elution stage of the technique is carried out under identical conditions as the precipitation stage and yet the blank is significantly increased from the mere (3.2 ± 3.0) cpd to the high (34 ± 27) cpd. The only major differences are due to the use of a cation exchange resin, a small plastic PP column, a much stronger acid (4 M instead of 0.2 M), and the increased amount of time required to execute. The regular exposure of the eluant in the reservoir during refilling, plus the potential for leaching and emanation from the column and the resin itself (because of the strong acid), must all contribute to the blank. Any contribution from leaching off of the column can feasibly be reduced by keeping the columns destined for use in the same 10% nitric acid bath as the filter holder assembly and the heatable beaker. With the small surface area available on the column, it is not expected to be a large source of background, although it shouldn't be ignored because of the strong acid it comes into contact with. The greatest surface area available to the acid is the porous polypropylene support disc which retains the resin. Order of magnitude calculations, based on emanation data by Uras et. al [63], show that the total amount of ^{222}Rn emanated from the polypropylene column and frit should only be about 5×10^{-3} atoms during the half hour that the 4 M nitric acid is in contact with the column. The number for ^{220}Rn is not known but may be comparable to within a few orders of magnitude, hence in either case the contribution is most likely negligible.

The two millilitres of resin itself must also contribute to the blank at some level, and unlike the column this has been investigated. A 0.29 g sample of untreated resin was alpha counted for six days with the result that (0.33 ± 0.24) cpd were observed above 7 MeV compared to the straight detector background of (0.380 ± 0.087) cpd acquired over nearly 50 days. Another 0.43 g sample of resin, which had been treated according to Step 1 and dried by IR for about 15 minutes, produced (0.67 ± 0.33) cpd over the same six day period. The treated sample doesn't agree with its respective straight detector background of (0.180 ± 0.060) cpd. In either case, the Dowex 50-X8 resin doesn't contribute very much to the background from an emanation point

of view. It remains to be seen if the low emanations from the resin are indicative of the levels which would be produced while elution is being carried out since there are two distinct physical processes occurring here. Because of the pretreatment of the resin in 4 M nitric acid, it was hoped that whatever the contribution to the blank was, it would have been effectively reduced by the cleaning process. The data seems to suggest otherwise, although the effect on the blank is essentially negligible. Cross contamination from one trial to another doesn't occur because virgin columns and resin are always used only once and discarded. There are therefore only two other possible sources which can contribute to the blank; the eluant, and the UPW itself. It is not expected that the acid itself, being of the ultrapure kind, would contribute above 0.01 counts per day. The UPW, used in greater quantities during precipitation alone cannot be the cause. Hence, what remains are the untreated columns, the Dowex 50-X8 cation exchange resin, and the repeated exposure to fumehood air as suspects. Reductions to the blank will most likely be achieved with greater control over these aspects of the elution procedure.

The lead recovery for the combined precipitation and elution procedures, from the data in table 4.7, is a respectable $(67 \pm 15)\%$. Although 67% is not what was hoped for, it may be possible to increase this number by oxydizing the EDTA as outlined (for which the drawback would most likely be an increase in the blank).

Examination of the ^{212}Pb source data for the paired E1 series tests in table 4.7 reveals some encouraging results. In spite of the lower stable lead recovery for the combined elution and precipitation procedure in E1A4 compared to precipitation only in E1B4 (figure 4.5), the ratio of the corrected total counts for the combined to single procedure agrees with similar ratios from the E1A5-E1B5 and E1A6-E1B6 pairs (figures 4.6 and 4.7 respectively). The ratios were found to be 104%, 98.1%, and 97.9% respectively. In these tests, the bubbler would be used to make a strong ^{212}Pb source in UPW only (about 10 Bq or so) which would be split into two equal halves. The halves were contained in 100 cc polypropylene graduated cylinders to which 10 mg of EDTA and 0.1 mg stable lead was added to one and 0.1 mg stable

lead plus nitric acid (to acidify to 0.2 M) was added to the other. Both halves would be precipitated but the one with EDTA would first be eluted. Once the two alpha sources were filtered and dried by IR lamp, they would be introduced and counted simultaneously in the alpha spectrometer. Good ^{212}Pb tracer ratios as high as those obtained are indicative of the successful application of a spike followed by its recuperation. The ^{212}Pb tracer matches the stable lead recovery, therefore the stable lead recovery can be used as a recovery indicator for low ^{212}Pb level work. The difference between the high 98.4% recovery for one precipitation and the high 70's for the other two may be due to plating, since the source was split prior to the addition of the EDTA or nitric acid, but this is unlikely due to the short time the lead was in solution without nitric acid. The stable lead recovery for the three elution runs (E1B4, E1B5, and E1B6) again shows that EDTA interferes with precipitation, although the recovery for the three runs agree as opposed to those of the blanks (NB1-5) which varied from 43.6% to 88.1%.

4.6 Reverse Osmosis

The last stage of the technique, reverse osmosis, serves to preconcentrate the few ^{212}Pb atoms found in the many tonnes of water down to a small manageable and practical volume. By adding EDTA (along with the 0.1 mg of stable lead carrier) at the 100:1 EDTA:Pb level in the water (and mixing well), the RO system can then extract the EDTA-Pb complex more efficiently. The EDTA's primary purpose is to complex the thorium for removal but it also serves to complex the lead for assay. The EDTA, it is expected, will also prevent any thorium or lead (from a radon daughter) formed in solution from plating onto the acrylic surface. Lead or Thorium which plate out onto surfaces or which remain as insoluble oxides on the same surfaces, would effectively evade removal or assay respectively. EDTA is best suited for preventing species from plating than removing already plated out species [55]. EDTA also has the advantages, at the level proposed for SNO, of not

Figure 4.5: Split ^{212}Pb source data for runs E1A4 and E1B4. The top graph was for precipitation only whereas the lower graph included elution as well with the new 250 cc water wash. The shift in the peak locations for the lower graph (corresponding to data acquired in chamber B of the spectrometer) is due to the use of the calibration data of the upper graph (acquired in chamber A).

Figure 4.6: Split ^{212}Pb source data for runs E1A5 and E1B5. The lower graph was for precipitation only whereas the top graph included elution as well with the new 250 cc water wash. The shift in the peak locations for the lower graph (corresponding to data acquired in chamber B of the spectrometer) is due to the use of the calibration data of the upper graph (acquired in chamber A).

Figure 4.7: Split ^{212}Pb source data for runs E1A6 and E1B6. The top graph was for precipitation only whereas the lower graph included elution as well with the new 250 cc water wash. The shift in the peak locations for the lower graph (corresponding to data acquired in chamber B of the spectrometer) is due to the use of the calibration data of the upper graph (acquired in chamber A).

contributing to the background, of having no effect on the pH of the heavy water, and not affecting radium extraction onto MnO_2 or thorium and lead extraction onto HTiO . It is just as important to prevent plate-out in the purification system. A measure of the stability and strength of the EDTA-Pb complex is its K_d or dissociation constant. The K_d for the EDTA-Pb complex is a rather high 1×10^{18} which is pH dependent (for thorium it is 1×10^{23}). A theoretical calculation based on gas kinetics (Michal Shatkay, personal communication) suggested that the 1 ppb of EDTA in the otherwise pure heavy water (along with 1 ppt of stable lead carrier) should be sufficient to complex the lead in under an hour. The calculation was meant only as an order of magnitude type calculation since the very low Pb-EDTA concentration in pure heavy water was approximated by gas kinetic theory for trace gases. Under these conditions, the lead in solution would almost certainly quickly form a highly stable EDTA-Pb complex (at the neutral pH 7 of the SNO heavy water) which could then be concentrated by RO down to a manageable volume. However, if impurities, such as Ni are present in the water, the availability of free EDTA molecules would become a limiting factor.

Reverse osmosis (also known as Hyperfiltration) [52] to be employed in SNO employs tightly wound spiral microporous polymer based membranes of pore sizes ranging from 0.1 nm to over 1 nm. In comparison, aqueous salt, metal ions, and atomic radii are in that range as well, hence the great ability for RO to clean water of dissolved impurities. The membranes were manufactured specifically for SNO and were designed to be of the highest possible bulk purity. The Kimura-Sourirajan analysis (KSA) model [52] for the reverse osmosis system is assumed since it is the recommended transport model for porous membranes under low concentration single solute conditions. The KSA model is based on a combined sorption-capillary flow mechanism whereby water is preferentially attracted to the membrane and forced through the pores by pressure. The solute (EDTA-Pb) dissolved in the solvent (UPW) is forced onto the membrane surface by the high pressure pump. The water which is forced through the membrane pores to the low pressure side is

called the permeate; the solute and solvent solution retained on the high pressure side of the membrane is called the retentate or concentrate. The separation is therefore defined as the ratio of the concentration of the solute on the permeate side to the concentrate side subtracted from unity. The osmotic pressure from the solute is simply

$$\Pi = C'RT \quad (4.1)$$

where C' is the molar concentration of solute in moles/m³, R is the gas constant (8.3143 J/moleK), T is the temperature in Kelvin, and Π is the osmotic pressure in Pascals. Equation 4.1 holds true for dilute systems only and is applicable in the case of lead assay because of the low concentrations involved which is in the sub- μ molar range (for one tonne of UPW). Due to the minute amount of solute in the solution, the pressure necessary for the operation of the RO is therefore not due to the osmotic pressure of the solute, but to the resistance of the membrane itself.

Tests carried out by Shatkay et al [58, 57] have shown that the separation of the EDTA-Pb complex is at the 98% level or better for a few membrane types for small scale [58] and large scale [57] tests. Lead ions alone, on the small scale tests, were recovered with efficiencies in the mid ninety percent. With added EDTA, the recoveries were all greater than 99.4%. The small scale tests were done with circular membrane coupons of 10.5 cm² area contained in a stainless steel pressure vessel, whereas the large scale tests were carried out on a commercially available eight inch diameter four foot long spiral wound membrane. A separation of 98% was measured in the presence of salt for one type of membrane tested; the Nitto 759 (made of an aromatic polyamide derivative), which was therefore chosen for use in the SNO heavy water system. The EDTA-Pb complex is actually at least five times larger than the lead ion itself which may explain the increased separation observed in the small scale tests.

The two stage reverse osmosis test rig (TRO) which was employed for the present work is shown in figure 4.8.

Figure 4.8: Diagram of the two stage reverse osmosis test system employed for the testing of the lead assay technique. All pipework and pressure vessels in the high pressure side are made of stainless steel.

Two large polypropylene one tonne tanks, called the One Tonne Test Facility (1TTF), were used to store the one or two tonnes of UPW needed. Large lids and a draped plastic sheet provided some protection against airborne dust. One tank would normally be filled while the other would serve to accumulate the permeate from the first stage RO unless two tonnes of UPW were desired. The UPW itself was generated by a larger commercial process RO system capable of producing a flow on the order of 120 litres per minute which would be piped to the 1TTF. The 1TTF had its own small pump to pump the water over to the large constant displacement high pressure pump that provided the necessary pressure to overcome the resistance of the large first stage membrane and what osmotic pressure may be found across it. Most lead recovery tests performed on the TRO were done with a single tonne of UPW which was put to drain rather than to the second tank.

A 500 cc UPW sample with 0.2 mg of stable lead carrier and 20 mg EDTA (from a stock of 100:1 EDTA:Pb) placed on the bubbler system overnight would constitute the spike stock for RO tests. Because of the shortcoming of the bubbler system thorium would also be part of the spike. No tests were made to determine the level of the thorium contamination present in the spikes. The EDTA in the spike was necessary to keep most of the ^{212}Pb in solution as EDTA-Pb. The spike would be split into two equal halves (the final data would be corrected for any asymmetry in the splitting). Mixing of the 250 cc ^{212}Pb source was done by simply recirculating the water in the tank for about five to ten minutes at the maximum flow rate of 25 lpm. The water removed from the bottom would be piped to the top about a meter above the water surface, thus providing ample mixing. The spike could then be recovered by the RO during which time the second half of the spike was eluted and precipitated. Once the RO spike had been recovered, eluted, and precipitated as well and when both precipitates were ready, they would each be placed in one of the two chambers of the α spectrometer and simultaneously counted for a period of 24 hours. By using identical SSB detectors, as near identical geometry as possible, and simultaneous counting, it was possible to simply compare the results by dividing the

total counts detected from the RO recovered source to the eluted and precipitated only source. On the assumption that the efficiencies were quite identical for both chambers of the counter, they would all tend to cancel out. The typical operating parameters observed during RO test runs are listed in table 4.8.

Although the tonnage of UPW was twice that normally used, the operating parameters remain the same. The input flow rate to the first stage pump always stabilizes to about 5.7 lpm because the high pressure pump is a constant displacement type. To maintain the concentrate from the second stage RO in as little a volume as possible, the concentrate bleeder valve is kept closed so that the retentate is recirculated in the fixed volume of the piping. Once all the UPW has passed through the first stage, the pressure drops and causes the pump to automatically shut off. Since the first stage pump also provides the pressure to run the second stage, its operation is simultaneously halted as well. Essentially, the spike is then found in the recirculation loops of the first and second stages. The estimated volume of the first stage recirculation loop from which the second stage RO feeds is about 15 l. During the period of operation of the TRO, the second stage RO samples about 18 l from the first stage recirculation loop. This represents a shortcoming because some of the spike is most likely left in the first stage concentrate loop when the TRO shuts down. The TRO has been modified since the tests reported in table 4.9 were done. A pump was added to the first stage recirculation loop to provide pressure for the second stage RO. This will allow all the concentrate from the first stage RO to be forced through the second stage one, thus recovering a maximum of the initial spike.

After the TRO shuts down, the second stage concentrate is forced off of the membrane and piping and collected in a PP bottle by pressurized nitrogen gas. Once the level in the bottle stops rising, the gas is turned off and UPW is forced back into the system to prevent the destruction of the membrane should it ever dry out. The volume of concentrate depends on the free volume in the second stage pressure vessel and piping, therefore it is a constant volume of about 360 cc

Stage 1

Time Index	Feed Press. psi	Syst. Press. psi	High Press. psi	Sys. Temp.	Recirc. Flow gpm	Conc. Flow lpm	Perm. Flow gpm
12:45	22	328	346	23	4	0.15	1.6
14:00	22	333	351	27	4	0.15	1.6
15:30	22	337	355	26	4	0.15	1.6
17:00	22	336	353	26	4	0.15	1.6
18:25	22	325	342	27	4	0.15	1.6
18:26	RO off						

Stage 2

Time Index		Conc. Flow cc/min		Sample Bleed cc/min		Pressure PSI	
12:45		131		-		107	
14:00		131		-		115	
15:30		131		-		120	
17:00		131		-		120	
18:25		131		-		117	
18:26	RO off						
18:29	N ₂ on						
19:20	N ₂ off						

Table 4.8: Typical operating parameters for the operation of the TRO systems' first and second stage. The data above was for a two tonne UPW water sample which had been spiked with 250 cc of UPW containing 0.1 mg stable lead (and ²¹²Pb from the bubbler) and 10 mg of EDTA. The sample bleed from the second stage was kept closed off. The N₂ gas purge is done at about 50 psi.

(compare with the spike volume of 250 cc). After the elution and precipitation has been performed the source or background level is then counted; the results for several runs are reported in table 4.9.

The first block of data reported in table 4.9 are blank measurements that were carried out with RO water for T9A3 and RO water that was also polished for the six other tests listed in that first block. The RO water in this case refers to UPW produced by a large process RO system and not the TRO. The polishing stage consists of a bank of mixed bed anion and cation exchangers through which the RO water is passed after production. The mixed bed exchanges H^+ and OH^- with charged impurities thus replacing the impurities with pure water. The lead recovery for T9A3 is not known; the 7.5% shown is an assumed recovery comparable to that found in tests carried out in the same time frame. Despite that, all blank runs indicate that the background level in the system is quite high for ^{212}Pb assay. Due to the very low nature of the recoveries it is also possible that the corrected total counts cannot be greatly trusted. Many more trials were attempted which are not shown in table 4.9 because they were aborted because of technical problems such as loss of concentrate through a leaking pressure release valve on the TRO, loss of concentrate during elution from disconnected tubing, or essentially anything that could go wrong during the execution of the three steps of the procedure (drying out of cation exchange resin, loss of precipitate during filtration, fire alarms and evacuation of the building, etc.). The average counts for the blank runs in the ^{212}Po peak (>6.1 MeV) is of the order of $(5.7 \pm 5.2) \times 10^2$ cpd which includes a bothersome high result (T9A5) which, it would seem, almost always occurs at least once. The RO blank of course already includes all contributions from elution, precipitation, and the counter system and thus represents the blank expected for the entire procedure as it could be applied in SNO. The recoveries measured by FAA also encompass all stages of the technique and are corrected for the spike FAA as well which are determined from analysis of samples of spike stock. With the blank and its variability as it stands, ^{212}Pb assay would not be possible at the single atom

Description of Test	Recovery Pb(%)	Total (cpd)	<6.1 (cpd)	>6.1 (cpd)	Corrected Total	<6.1 (cpd)	>6.1 (cpd)
T9A3-UREP	7.5*	32	19	13	4.3×10^2	2.5×10^2	1.7×10^2
T9B4- REP	4.9	38	13	25	7.8×10^2	2.7×10^2	5.1×10^2
T9A5- REP	19.7	387	57	330	2.0×10^3	2.9×10^2	1.7×10^3
T9B5- REP	36.5	100	36	64	2.7×10^2	9.9×10^1	1.7×10^2
T9A6- REP	10.2	70	23	47	6.9×10^2	2.3×10^2	4.6×10^2
T9B6- REP	13.3	116	42	74	8.7×10^2	3.2×10^2	5.5×10^2
T9A7- REP	5.6	32	9	23	5.7×10^2	1.6×10^2	4.1×10^2
T9A1- P	25.0	3226	1142	2084	1.3×10^4	4.6×10^3	8.3×10^3
T9B1- REP	16.3	1927	705	1222	1.2×10^4	4.3×10^3	7.5×10^3
T9A2- P	32.6	458	176	282	1.4×10^3	5.4×10^2	8.6×10^2
T9B2- REP	3.4	87	34	53	2.6×10^3	1.0×10^3	1.6×10^3
T9B3- P	-	1741	612	1129	-	-	-
T9A4- REP	-	1920	661	1259	-	-	-
E1A7- P	90.2	29404	10931	18473	3.2×10^4	1.2×10^4	2.0×10^4
E1B7- REP	29.9	5511	2150	3361	1.8×10^4	7.2×10^3	1.1×10^4
E1A8- P	92.8	30983	10993	19990	3.3×10^4	1.2×10^4	2.1×10^4
E1B8- REP	42.8	5401	2181	3220	1.3×10^4	5.1×10^3	7.5×10^3

Table 4.9: Listed is the relevant α data for several blank and split source spike runs on the TRO system. Whenever the acquisition time wasn't 24 hours, the total number of counts were corrected for this. The three rightmost columns were corrected for the stable lead recovery efficiency listed which was determined by FAA analysis on the precipitate after the spectrum had been acquired. The <6.1 MeV column represents the 6.09 MeV α from ^{212}Bi decay (BR=36%) and the >6.1 MeV column is the 8.78 MeV ^{212}Po α decay (BR=64%). * The lead recovery has been estimated to be between 5 and 10% for T9A3; no FAA analysis of the ppt was made at the time. The units cpd are counts per day.

per tonne level where only about 12 counts are expected in the ^{212}Po peak (for a 240 tonne sample of heavy water).

The blank from the RO is considerable and definitely must be reduced. The possible sources of the background levels observed should therefore be investigated. Some light can be shed onto the problem by considering the history of the 1TTF which contained and fed the UPW to the TRO system. Parallel to the lead work, radium extraction tests were carried out with MnO_2 columns and ^{224}Ra spikes which also used the 1TTF for storage of the spiked UPW. The ^{224}Ra spikes were made from a 7 M HNO_3 solution containing both ^{228}Th and ^{224}Ra in equilibrium from which radium was preferentially extracted by absorbing the negatively charged thorium nitrate complex onto an anion exchange resin (M. Shatkay, personal communication). The ^{224}Ra spikes nevertheless contained less than 1 per ml of thorium which has a half-life of 1.9 years. Spikes added to UPW in the 1TTF would then partly plate out onto the walls of the tanks where the thorium would also accumulate due to its long half-life. As the thorium decays, the daughters eventually come into equilibrium, and these daughters include ^{220}Rn and ^{212}Pb . Emanation of the radon into the water would give rise to supported ^{212}Pb that would be picked up by the EDTA in the spike for the blank runs. It is not expected that there would be much radon emanated during the short time the freshly purified water was in the tank. A 0.2 Bq radium spike would contain less than 0.0002 Bq of thorium which, for 50 tests, would have a total activity of less than 0.01 Bq and would give rise to at most 36 decays per hour. The thorium contamination of the radium spikes alone cannot account for the high backgrounds measured for the full procedure which are in the several hundred counts per day range. Following a similar analysis for contamination of the bubbler-made ^{212}Pb spikes, which are usually on the order of 10 Bq, the thorium contamination level for about 10 tests is 360 decays per hour, assuming 0.1% of the thorium spike is blown out into the bubbler from the MnO_2 fines. The high blanks observed for the RO system would then be partly due to the thorium contamination that plated onto the walls and membrane from the spike

made in the bubbler system.

Thorium spikes are not expected to be the only source of background contributing to the blank. Since all materials contain some amount of ^{232}Th , however small, leaching from the inner surface and emanation of radon from a little deeper still will be a source. Very large surfaces such as the reverse osmosis membrane itself, of about 7.9 m^2 , even if it has a high bulk purity, may contribute to the blank, especially at the level of one atom per tonne of water. Other sources include the stainless steel pipes, pressure vessel, and the rest of the TRO system. No reverse osmosis tests were carried out after the elution procedure had been modified to satisfactorily remove EDTA, hence the absolute lead recovery for the RO stage of the technique cannot be given. All the data presented in table 4.9 is plagued with the adverse effects of too much residual EDTA after elution of the concentrate taken from the TRO. Since the aforementioned tests were conducted, new one tonne tanks were installed on the reverse osmosis system and no ^{224}Ra spikes (not even ^{212}Pb ones) have been in contact with the walls. The system has also been thoroughly washed prior to the exchange of the previous membranes for new ones which were never subjected to radioactive spikes. Therefore, a series of blank measurements with 100:1 EDTA:Pb spikes (0.1 mg stable lead only) would simultaneously determine both the blank and the stable lead recovery (by FAA) that is required for the technique.

Besides contamination from thorium spikes, the high background signals could also originate in part from the polisher. Over time, the polishing unit manages to accumulate large quantities of ions by removing from the water divalent ions (of which some must be thorium) and replacing them with monovalent ones. When the thorium decays, its radon daughter is eventually produced and some of the radon atoms emanate into the water flowing through the unit thus entering the 1TTF. The polisher behaves like a source under these circumstances. To test this idea, two tests were done with polished UPW; the first tested the water immediately after production while for the second, before it was carried out, the water was left

sitting for six days to let any ^{212}Pb that might have come from the polisher decay away. In table 4.9, tests T9B4 to T9B5 made immediate use of the UPW whereas tests T9A6 to T9A7 made use of the water only after an idle waiting period of six days. For the first series of measurements which were actually performed first, the water was passed through the TRO almost immediately after its manufacture. Some four hours later, the same tonne of water was respiked with EDTA and stable lead carrier as initially and again passed through the TRO to the other empty tank of the 1TTF. After having sat overnight, the water was again spiked and passed through the TRO (but to drain this time). The second series of tests were conducted in the same fashion except that the UPW was manufactured and spiked six days ahead of time.

The differences in the two sets of measurements may be interpreted as follows. In the second series tests, any ^{212}Pb (initially released as ^{220}Rn by the polisher) would have definitely decayed away because of the over 12 half-lives between its production and its assay, hence any observed signal would be from the 1TTF and TRO systems. The relatively constant rate measured implies that the ^{212}Pb is supported by a long lived parent such as ^{228}Th ($t_{1/2} = 1.9$ years). Had the contamination been from ^{224}Ra , it would have had enough time to decay away considerably between the two tests, yet the level in the second series is actually higher. The first series tests, on the other hand, show a marked increase in counts for the second pass, followed by a marked decrease for the following day. The third pass data for the first series tests is actually twice that expected from the counts of the second pass. This may be due to the building up of ^{212}Pb from thorium in the tanks (or maybe even from one tank in particular). The much larger result of the second pass compared to that of the first pass is puzzling. Because the radon parent of ^{212}Pb has only a half-life of 56 seconds, it is not expected that more than several minutes are required for the lead to build up to its maximum activity before the activity level starts to decrease. The activity level decreases with time in this case since the ^{212}Pb isn't supported. The radon had more than ample time to decay away completely to lead during the

first several minutes of the initial pass: this same pass should have had the largest count rate compared to the second pass. The reason behind this discrepancy may be that one tank in particular was contaminated and gave rise to the high second pass counts of the first series test. The near constant count rates observed six days later would simply be due to the contamination again re-establishing equilibrium. Although this was not investigated any further, the data showed that there was possibly a source in the tanks and from the polishers. In an actual three stage RO run for lead assay in SNO, there wouldn't be any spiked components in the procedure and the use of polishers is an option. The contribution to the blank from the TRO was not isolated, and it is believed that a portion of the actual blank was from the 1TTF.

Of some concern as well are the two abnormally low stable lead recovery results for the precipitation stage alone of T9A1 and T9A2. No EDTA was present in the spikes for these two tests for which no explanation could be found as to their lower recoveries. Normally the stable lead recovery for precipitation alone is $(98.0 \pm 3.5)\%$ which is not prone to large unexpected variations as evident in table 4.2.

The data presented in the lower half of table 4.9 are from runs with split ^{212}Pb sources. Despite having their share of problems, these runs were intended to show that ^{212}Pb spikes could be recovered from one tonne of water. By taking the data in the appropriate P-REP pairs and calculating the ratio of the total efficiency corrected counts of the RO+Elution+Precipitation (REP) to precipitated (P) only runs, the efficiency with which the spike was recovered can be determined. The first pair (tests T9A1 and T9B1) yields 88%. The subsequent pairs give rise to efficiencies of 145%, 78%, 54%, and 38% respectively when the RO measurement of each pair has been corrected for the average background of 570 counts per day. The data for the E1A7 and E1B7 pair of runs is shown in figure 4.9. The very low stable lead recovery (3.4%) of T9B2 most likely explains why the radioactive lead tracer is overestimated. The lack of support from an FAA analysis of the lead recovery for the T9B3-T9A4 pair renders that measurement of 78% suspect. Although the first

two pairs of measurements represent only two tests, the results are encouraging as to the level of ratio of radioactive tracer expected which may be 88% or greater. Eventhough the stable lead recoveries were relatively low, the spectra once corrected for the differing recoveries would give a radioactive lead tracer ratio close to unity. This implies that the stable lead recovery is a good tracer for the radioactive lead. Several more measurements would be needed to confirm these preliminary results.

Despite the relatively high radioactive lead tracer ratios obtained, the two low numbers of 54% and 38% (corrected for stable lead recovery) can be explained in light of the MnO_2 fines problem [19] and also in light of the persistence of EDTA interference with precipitation. The E1A7-B7 and E1A8-B8 test pairs were conducted just after the membrane setup was used in a ITTF experiment where an attempt was made to measure the ^{212}Pb signal which might have been left over from a radium extraction experiment onto MnO_2 beads. The three trials carried out earlier were done prior to this co-operative effort. Because the same water that had seen the MnO_2 was employed on the RO system, the fines were caught in the system and especially on the RO membrane. Despite the ample rinsing of the RO system thereafter, it is suspected that enough fines remained to absorb part of the stable lead carrier, which accounts for the low stable lead carrier recovery for E1B7 and E1B8 (determined after precipitation). Evidence of the fines was observed when in the final stages of precipitation the lead chromate solution, which filtered through the polysulfone filter much more slowly than usual, would no longer permeate through the filter after about 10% of the total volume had been passed through. Attempts to observe by Scanning Electron Microscope what clogged the filter revealed nothing on the surface of the filter, which was also abnormally sparsely populated with lead chromate crystals. The presence of MnO_2 fines does not, however, explain the lower radioactive lead tracer ratios compared to the stable lead recovery ratios. The interference from EDTA would also decrease the stable lead recovery, similarly to the MnO_2 fines, during precipitation as it would the radioactive tracer recovery. The ratio of stable lead recovery (REP/P) from table 4.9 was 0.33 and 0.46 for the E1A7,

Figure 4.9: Split ^{212}Pb source data for runs E1A7 and E1B7. The top graph was for precipitation only whereas the lower graph included elution (with the new 250 cc water wash) and reverse osmosis as well. The shift in the peak locations for the lower graph (corresponding to data acquired in chamber B of the spectrometer) is due to the use of the calibration data of the upper graph (acquired in chamber A).

E1B7 and E1A8, E1B8 pairs respectively as opposed to the ratios of 0.19 and 0.17 respectively for the uncorrected total radioactive tracer. Other than the abnormal conditions under which these tests were carried out, there is no explanation as to why the radioactive tracer ratios are lower than those of the stable lead. The first two tests carried out prior to the introduction of MnO_2 fines into the TRO showed ratios of 0.65 and 0.10 for stable lead and 0.60 and 0.19 for radioactive lead. There is no sizable discrepancy in the first test where 0.65 compares favorably with 0.60, which gave a very acceptable corrected radioactive tracer ratio of 88%, and despite the factor of two discrepancy evident for the second test with 0.10 compared to 0.19, once the corrections were made to the counts, the tracer ratio was 145%. It is not understood why this discrepancy exists only after MnO_2 fines were introduced into the TRO since MnO_2 does not have a preference for radioactive lead over stable lead: from a chemistry point of view, a difference in the chemistry between different isotopes of lead is not expected.

In light of the data presented, the assay of ^{212}Pb by reverse osmosis preconcentration is feasible, provided that the blank level of the procedure can be considerably reduced to a suitable level of something less than the expected twelve counts for ^{212}Po . This may prove to be difficult if, once all other external sources have somehow been eliminated, the bulk purity of the RO membrane itself gives rise to a high blank. The membranes employed for the tests in this thesis were already manufactured to SNO specifications in the first place, so there may be little room for improvement in that respect.

4.7 Synopsis of All Results

All the efficiencies and background levels found for the various ^{212}Pb assay procedure stages are presented below in table 4.10.

Although the stable lead recovery by mass balance for reverse osmosis has not been measured by the author, the stable lead separation was however independently

Parameter	Spectrometer	Precipitation	Elution	Reverse Osmosis
Blank	0.27 ± 0.16	2.9 ± 3.0	31 ± 27	540 ± 510
% Pb	-	98.0 ± 3.5	68 ± 14	98% separation/stage
% of 4π	25	-	-	-

Table 4.10: ^{212}Pb assay technique parameters. All blank levels are quoted in counts per day. Blanks and efficiencies have all been uncoupled and therefore are listed as intrinsic values for each stage.

determined to be about 93% [57] per stage. An overall lead recovery efficiency can therefore be calculated to be on the order of 65% for two stages of reverse osmosis. A third stage of reverse osmosis would reduce the overall efficiency to about 64%. In comparison to the elevated precipitation and reverse osmosis efficiencies, the one for elution is the cause for the lower overall efficiency, and this is all due to the residual interference of EDTA in the precipitation stage. If an increased recovery is desired, then more work needs to be done in trying to eliminate the EDTA prior to precipitation. Care must be taken in doing so to avoid causing an increase in the blank which would be most detrimental.

The efficiency of the detector is quite low at 25% and this number is not expected to vary by more than a few percent from the small variations in the geometry that occur when positioning sources. The greatest potential for improvement lies with the detector although again one must be wary of the effect on the blank if any improvements might have. Afterall, the blank and its variability is what really determines the level of sensitivity of the technique.

The level of the blank, coupled to all other subsequent stages of the procedure, is a hefty 570 ± 520 cpd. This number is by no means the lowest attainable for the technique since no effort has yet been made at the reverse osmosis stage to reduce it or to remeasure it since the TRO system has been cleaned and fitted with a new

(and clean) 1TTF. Despite the level that can be attained, the blank is what in essence determines the sensitivity of the technique. By taking into account all the listed efficiencies and combining them with the full procedural blank of the TRO, the number of counts detected actually translates to $(3.6 \pm 3.2) \times 10^3$ cpd. This represents $(4.7 \pm 4.2) \times 10^3$ ^{212}Pb atoms collected from 1 tonne of UPW. Assuming for the sake of the calculation that the ^{232}Th chain is in equilibrium, the level of ^{212}Pb detected translates to a sensitivity of $(10.4 \pm 9.2) \times 10^{-12}$ g(^{232}Th)/g(UPW). At that level, the lead assay technique is just less than 3500 times less sensitive than required! It is expected, since most of the blank may be due to a contaminated 1TTF, that the actual blank from the TRO system alone may be one or two orders of magnitude less. To simply be at the 3×10^{-15} g/g level for a 1 tonne test, the blank shouldn't be more than 1 cpd. Obviously, tests on a single tonne or two cannot be made at the same sensitivity because the blank for elution, precipitation, and the detector is already in the 34 cpd range, and this is a factor of 34 too large. Therefore, in its present state, the lead assay procedure cannot provide a 10% determination of the ^{212}Pb content of the SNO heavy water.

Chapter 5

Conclusion

5.1 A Comparison of The Various Assay Techniques Developed for SNO.

In light of the results obtained for the lead assay technique, a comparison can be made with the other techniques which were developed to assay the ^{232}Th and ^{238}U chains. The details of these alternate and competing techniques were given in section 3.4, thus only the ultimate efficiency, blank, and sensitivity are presented in table 5.1.

For any technique to reach its goal of a 10% measurement, the sensitivity must be 10% of the required purity level for the chain in the medium the method was devised to assay. The heavy water for example must be cleaned to the level of 3×10^{-15} g/g, therefore any technique for its assay must have a sensitivity of 3×10^{-16} g/g to give a 10% measurement of the purity. The sensitivities listed in table 5.1 represent $3.5 \times 10^5\%$, 43%, 17%, 7%, and 123% respectively compared to the desired 10%, where the Lucas Cell (and second Electrostatic listing) results were compared to 3×10^{-15} g(^{238}U)/g(UPW). In all cases the UPW assumed is heavy water. The Lucas Cell may be a factor of two worst than indicated since its use at Carleton has demonstrated that the background level is more like 40 Rn decays/day (H. Lee,

Technique	Efficiency	Blank	Sensitivity
²¹² Pb Assay	64% × 25%	570 cpd	1.0×10^{-12} Th
Cryodetector	64 × (Ra-Ext)%	2 Rn/day	1.3×10^{-15} Th
Electrostatic	40%	-	5.0×10^{-16} Th
Electrostatic	40%	-	2.0×10^{-16} U
Lucas Cell	33%	20 Rn/day	3.7×10^{-15} U

Table 5.1: A comparison of the parameters which define the assay techniques which may be used at SNO. The sensitivity is in $\text{g}(^{232}\text{Th})/\text{g}(\text{UPW})$ except for the Lucas cells and second listing for the Electrostatic counter which is in $\text{g}(^{238}\text{U})/\text{g}(\text{UPW})$. The overall efficiency of the Cryodetector must also be coupled with the Ra extraction efficiency as noted.

personal communication). Only one technique comes very close to succeeding for Th, and that is the Electrostatic counter, and it fares very well with the ²³⁸U chain as well. All the other techniques can still be of use even though the sensitivity isn't as great. To obtain a better determination with lesser sensitivity, these techniques would have to make consecutive assays which when combined would give a time averaged result of greater sensitivity. The lead assay sensitivity is by far the worst with the technique in its present state of development.

For the Lucas Cell, a five tonne water sample was assumed for the calculation, thus the sensitivity may change if the blank increases from that shown for an actual measurement. The Cryodetector and the Electrostatic counter sensitivities are also based on an equivalent water sample of 100 tonnes which could be assayed at 20 lpm, for example, requiring about 17 hours. The α counting of the radon daughters afterwards would take 15 to 20 days for the Cryodetector, 11 days for the Electrostatic counter, and 10 days for the Lucas Cell (which also employs three separate cells). The sample size of the UPW assayed by these techniques is essentially governed by the MnO₂ column design, size, and efficiency. To sample a larger volume of water without linearly increasing the time required, larger columns are needed with a greater MnO₂ capacity. This is necessary to ensure that the residence time

of the radium atoms in the MnO_2 bed is adequate to maintain a high extraction efficiency. Twenty and 200 lpm are the two available flow rates for column extraction whereas lead assay is done solely at 200 lpm. The assay of 240 tonnes of water is possible for the lead assay because it is simply a matter of running the RO for the appropriate amount of time of 20 hours at 200 lpm. If the lead was supported by thorium for example, then in essence larger samples could be taken to increase the amount of ^{212}Pb accumulated. The fact that the lead assay only requires a 24 hour counting period means that daily measurements could be made. A 20 hour RO run and about four hours of chemistry roughly equal the 24 hour counting period employed, hence a new sample could be taken and processed while the previous one is being counted. This would enable the daily tracking of the ^{232}Th background levels in the heavy water, provided of course that the technique can be improved to meet the sensitivity requirement.

At first glance, lead assay seems hopeless. Upon closer inspection of the issues, the technique doesn't seem that bad after all. The blank presented in table 5.1 was obtained from a system which had regularly seen spikes of ^{224}Ra containing very small amounts of ^{228}Th . It also used large tanks which would not be as clean as the actual AV is to be. The heavy water itself is expected to be very clean and at or near the 3×10^{-15} g/g level of thorium once purified, which leaves only the RO system to contribute to the blank. What comes off the acrylic vessel and what is found in the water in terms of ^{212}Pb constitutes what must be measured and is not part of the blank: only the RO system and the chemistry procedure determines the blank. By realizing that most of the large blank comes, not from the water itself, but from the tanks and the RO, the true blank level is therefore less than what has been quoted. The sample size with which the blank was measured was only one tonne, with a 288 tonne sample the sensitivity will increase by a factor of 288. In essence, the RO system remains the same so the blank from it would be similar; the only differences are the increased flow rate and the increase in time of operation. A reduction of only a factor of 12 is then needed in the blank for

the lead assay technique to have a signal to blank ratio of 1:1 (100% sensitivity). A reduction of 12 in the blank may very well be possible, thus making lead assay viable. A reduction of 120 is needed to make a 10% measurement and may not be possible since this implies a blank of less than 5 cpd. At 5 cpd, the blank is comparable to that of the precipitation procedure and the α counter together. The elution procedure increases the blank by almost an order of magnitude by itself. There may yet be room for reduction of the elution's blank contribution although an order of magnitude seems doubtful.

Most of the contributions to the background levels from the radium based techniques come from leaching of thorium and radium and emanation of radon from the materials involved such as stainless steel pipes and aluminum chambers. External radon also contributes by diffusing through the pipes to some degree. In comparison, the lead assay technique has a larger piping network of the same material. None of the other techniques have the column exposed to air; in all cases, the columns will be connected to the cover gas system to avoid being in contact with air. Even the drying stage will be done via the cover gas system. The lead assay, on the other hand, cannot be carried out in anything else other than laboratory air and the concentrate solution is in direct contact with air for hours, not unless it is done inside a combination glovebox-fumehood arrangement. Under such conditions, nitrogen gas can be used but the fumehood cannot be part of the cover gas system because of the corrosive vapors that would be mixed in. This would certainly help reduce the blank due in part to the ^{212}Pb found in fumehoods of any kind and would effectively increase the sensitivity of the technique.

Evidently, lead assay doesn't fare well compared to the Cryostatic, Electrostatic, and Lucas Cell techniques under its present form. A much lower blank is required to improve the technique and there is a definite possibility that this can be achieved with the improvements that were proposed throughout chapter 4, although the ultimate level achievable is unknown.

5.2 Conclusion

As a technique, lead assay via reverse osmosis, elution, precipitation, and alpha counting is quite involved compared to the radium/radon based ones developed by others. The counting system itself accounts for (0.27 ± 0.16) cpd of background in the 6.1 to 9 MeV energy range. It is expected that this is an effective minimum unless drastic and costly measures are taken to isolate the alpha spectrometer from radon and dust laden air. Little improvement is expected to come of any further attempts to reduce the blank for the counter, and at the level it is presently at, any differences would not be noticeable.

The precipitation stage which comes just prior to the counter, may yet be improved, although the effect on the blank will be small. The changes to the procedure mainly require eliminating the contact of the equipment, reagents, and the assay solution with the radon and ^{212}Pb laden air. It was shown that despite the use of a highly efficient fumehood fitted with HEPA filters for dust removal (to class 100 specifications), enough ^{220}Rn and ^{212}Pb activity was being circulated in the clean air to swamp the background levels that were measured by almost two orders of magnitude. The measured blank for precipitation alone was found to be (2.9 ± 3.0) cpd which, when combined with the counter background, yields (3.2 ± 3.0) cpd in the same energy range. The stable lead recovery was found to be $(98.0 \pm 3.5)\%$ from combined gravimetric and FAA analysis of the precipitate recovered compared to the amount in the initial spike. There is essentially no room for improvement with the stable lead carrier recovery. Where there is the greatest room for improvement on the blank is in the elution and reverse osmosis stages.

Elution, which is carried out in the same fumehood and just prior to precipitation, must be investigated further in terms of the contribution to the blank from the cation exchange resin employed. As an added precaution, the column which contains the resin should also be stored before its use in a 10% nitric acid solution to help clean the outermost layer of plastic of thorium, radium, or radon which

might leach or emanate out into the resin. The blank obtained for the elution stage was (31 ± 27) cpd which when combined yields a cumulative blank of (34 ± 27) cpd. Despite attempts to elute the EDTA before the lead sample, ample amounts of it remain and is eluted along with the lead carrier and effectively persists in causing problems with precipitation. The highest recovery obtainable with a simple increase in volume of the UPW elution step (to remove as much EDTA as possible) was $(67 \pm 14)\%$. Oxidation of the EDTA may allow the lead recovery to be in the high ninety percent range, but not without possible adverse effects on the blank. As suggested earlier, a fumehood which uses nitrogen gas might help eliminate most of the radon and ^{212}Pb which is in the air. This would then reduce the risk of increasing the blank during the added oxidation step and might effectively render that added step feasible from the blank point of view.

The first stage of the technique is the reverse osmosis procedure, and this is where the greatest gains may be achievable. The lead separation from a single RO stage was measured independently [57] as 98%, which for three stages when combined with all other procedures in the technique gives a final recovery of about 64% for the entire technique (which doesn't include the 25% geometric α -counter efficiency.) The recovery on the TRO system was not determined gravimetrically (i.e., by mass balance) but rather by comparison of the concentration of stable lead in the permeate to that in the concentrate across a large 2.44 meter long coiled membrane. The 98% recovery quoted for the TRO cannot strictly be multiplied with the other procedure efficiencies, hence the 64% quoted may be too high or too low. There is most likely no room for great improvement here, despite the lack of a real mass balance analysis. Where the real improvement is expected is in the reduction of the blank. The blank, as measured under less than ideal conditions, was found to be $(5.7 \pm 5.2) \times 10^2$ cpd. This number is extremely high and it is suspected to be due to the possible contamination of the tanks used for storage of the UPW. Since no tanks would be part of the assay technique if used in situ, the blank most likely will come down. By also keeping the contents of the sample

bottle under cover gas, a small reduction in the blank might be gained. The effect of the TRO itself on the level of the blank is not known and should be investigated as this may be the largest contribution to the blank (due to the very large surface area of the RO membrane). Tests with 0.1 mg of carrier carried out under clean blank conditions would permit the determination of the new blank level (because the TRO system has now been cleaned thoroughly) as well as the true lead recovery by mass balance via FAA analysis.

In order to compensate for the losses in stable lead throughout the technique, an actual 100:1 EDTA:Pb spike in the heavy water should contain 0.16 mg and not 0.1 mg of carrier. This is necessary because the 0.1 mg of carrier is effectively a lower limit in lead mass which permits the efficient precipitation of the lead. Any amount very much less than 0.1 mg at the precipitation stage would considerably hinder the crystal forming process and reduce the actual lead recovery well below the present 98% level. Starting out with more carrier than necessary will ensure that in the end enough will have been recovered. The lead recovery must also always be determined by FAA since the mass of lead employed to begin with is a mere 0.1 mg, an amount which is difficult to tare accurately to less than a ten percent error.

The several repeated measurements of the blank for precipitation, elution, and reverse osmosis have shown, besides how high they actually are, that there is considerable variability in the results. Trying to reduce the fluctuations in the blank would require controlling virtually all aspects of the environment wherein the blanks were measured. Any attempt to do so would undoubtedly fail due to the difficulty in controlling such things as leaching and emanation. Even at the low levels at which these phenomena occur, their sum represents a contribution to the blank which is at least comparable to the twelve decays expected in the α -counter from an ultrapure heavy water sample of 288 tonnes. What remains to be done, since maintaining the blank constant is virtually impossible, is to reduce the level of the blank for which the variability will also be reduced. Despite how low the blank may become, it would be prudent to regularly measure it in order to track it and

its variability with time: unexpected events may trigger transient increases in the blank.

The present sensitivity is a factor of 3500 times too low compared to the objective of 3×10^{-15} g/g. For a 1 tonne sample the deduced sensitivity of 1.0×10^{-11} g(^{232}Th)/g(UPW) may come down to 3.4×10^{-14} g/g for a 288 tonne water sample, provided the blank doesn't increase. A more in depth analysis of the blank contribution from the reverse osmosis membranes is necessary. It is expected that the present blank level of 570 cpd was mainly due to contaminated storage tanks and the RO membrane itself. At 3.4×10^{-14} g/g, the technique would only be a factor of 12 away from being capable of rendering 1:1 signal to blank measurements for a signal at 3×10^{-15} g/g. There is promise in the idea that this could be achieved which implies a new and improved blank level of (48 ± 43) cpd. Whether or not this level can be achieved remains to be seen. Limiting the SNO NC background to 10% of its signal meant no more than 3×10^{-15} g(^{232}Th)/g(D₂O) and a 10% determination of that background level implies a sensitivity of 3×10^{-16} g/g. It is highly doubted that such a sensitivity could be achieved for lead assay because this represents a blank of no more than (4.8 ± 4.3) cpd. The precipitation and counting procedures alone amount to slightly less than that level.

All the other assay techniques, which are also all dependant on radium extraction and radon emanation, have been shown to be sensitive enough even if not at the 10% level desired. None of the radionuclide chains are expected to be in equilibrium because of the disturbance in the local environment construction has caused, and because of the mobility of radon which is one of the daughters in the chains. Radon which comes off of the AV or which enters the purification system by diffusion will throw the chains out of equilibrium by increasing the actual background level in the heavy water. Radium assay therefore measures the chains just prior to the radon input which causes the disequilibrium, hence the chain activity is underestimated. The lead assay technique was developed to be able to measure the chain activity below the radon to measure the level of disequilibrium. It is essential that this be

done whether by lead assay or other techniques. Lead assay in its present form of development is not sensitive enough to be useful in measuring the NC background, although it is expected that with the anticipated improvements to the blank it may be useful in a more limited 1:1 signal to blank capacity.

Bibliography

- [1] J.N. Abdurashitov et al. Results from sage (the russian-american gallium solar neutrino experiment). *Physics Letters B*, **328**:234–248, 1994.
- [2] E. Kh. Akhmedov. Resonant amplification of neutrino spin rotation in matter and the solar-neutrino problem. *Physics Letters B*, **213**(1):64–68, 1988.
- [3] P. Anselmann et al. Solar neutrinos observed by gallex at gran sasso. *Physics Letters B*, **285**:376–389, 1992.
- [4] P. Anselmann et al. Gallex results from the first 30 solar neutrino runs. *Physics Letters B*, **327**:377–385, 1994.
- [5] C. Arpesella et al. Borexino proposal, 1991.
- [6] A. Ashton and R. Chan. Monitoring of microgram per litre concentrations of trace metals in sea water: the choice of methodology for sampling and analysis. *Analyst*, **112**:841–844, 1987.
- [7] John N. Bahcall. Solar neutrinos i: Theoretical. *Physical Review Letters*, **12**(11):300–302, 1964.
- [8] John N. Bahcall. *Neutrino Astrophysics*. Cambridge University Press, New York, 1989.
- [9] John N. Bahcall. Two solar neutrino problems. *Physics Letters B*, **338**:276–281, 1994.

- [10] John N. Bahcall, Walter F. Huebner, Stephen H. Lubow, Peter D. Parker, and Roger K. Ulrich. Standard solar models and the uncertainties in predicted capture rates of solar neutrinos. *Reviews of Modern Physics*, **54**(3):767-799, 1982.
- [11] John N. Bahcall and M. H. Pinsonneault. Standard solar models, with and without helium diffusion, and the solar neutrino problem. *Reviews of Modern Physics*, **64**(4):885-926, 1992.
- [12] John N. Bahcall and Roger K. Ulrich. Solar models, neutrino experiments, and helioseismology. *Reviews of Modern Physics*, **60**(2):297-372, 1988.
- [13] Ed Baier. Literature survey on methods of storage and handling of trace analysis samples. unpublished, 1993.
- [14] John Christian Bailar. *Chemistry with Inorganic Qualitative Analysis*. Pergamon Press, Oxford, third edition, 1989.
- [15] A. J. Baltz and J. Weneser. Effect of transmission through the earth on neutrino oscillations. *Physical Review D*, **35**(2):528-535, 1987.
- [16] A. J. Baltz and J. Weneser. Matter oscillations: Neutrino transformation in the sun and regeneration in the earth. *Physical Review D*, **37**(12):3364-3377, 1988.
- [17] A. J. Baltz and J. Weneser. Implication of gallium results on the possibility of observing day-night matter oscillations at sno, super-kamiokande, and borexino. *Physical Review D*, **50**(9):5971-5979, 1994.
- [18] H. A. Bethe. Energy production in stars. *Physical Review*, **55**:434-456, 1939.
- [19] Ira Blevis. Large scale extraction, emanation, and fines using mno_2 . Technical Report SNO-STR-94-045, Center for Research in Particle Physics, 1994.

- [20] Ira Blevis, Ferenc Dalnoki-Veress, and Cliff Hargrove. Charge current event topology. Technical Report SNO-STR-95-001, Center for Research in Particle Physics, 1995.
- [21] Emanuel Bonvin, Andre Hamer, and Bhaskar Sur. The cryostatic detector. Technical Report SNO-STR-93-066, Center for Research in Particle Physics, 1993.
- [22] Emanuel Bonvin, Andre Hamer, and Bhaskar Sur. A si detector cryotrap as the counting device for water radioactivity monitoring in sno. SNO technical report, 1993.
- [23] Herbert H. Chen. Direct approach to resolve the solar-neutrino problem. *Physical Review Letters*, **55**(14):1534–1536, 1985.
- [24] Donald D. Clayton. *Principles of Stellar Evolution and Nucleosynthesis*. McGraw-Hill, Inc., 1968.
- [25] M. T. Crespo, J. L. Gascon, and M. L. Acena. Procedures for the assay of alpha-particle emitters in water samples. *Applied Radiation and Isotopes*, **43**(1/2):19–28, 1992.
- [26] Raymond Davis Jr. Solar neutrinos ii: Experimental. *Physical Review Letters*, **12**(11):303–305, 1964.
- [27] Raymond Davis Jr., Don S. Harmer, and Kenneth C. Hoffman. Search for neutrinos from the sun. *Physical Review Letters*, **20**(21):1205–1209, 1968.
- [28] George T. Ewan et al. The sudbury neutrino observatory proposal, 1987.
- [29] George T. Ewan et al. Sudbury neutrino observatory, collection of annexes in support of the main proposal, 1987.
- [30] Gordon Fraser. Japan super-kamiokande. *CERN Courier*, **34**(9):13, 1994.

- [31] Lars Hallstadius. A method for the electrodeposition of actinides. *Nuclear Instruments and Methods in Physics Research*, **223**:266–267, 1984.
- [32] C. Hammerton and J. G. Sherratt. *Analysis of Raw Potable and Waste Waters*. Great Britain Department of the Environment, 1972.
- [33] K. S. Hirata et al. Real-time, directional measurement of ^8B solar neutrinos in the kamiokande ii detector. *Physical Review D*, **44**(8):2241–2260, 1991.
- [34] A. J. Howard. Method for radioassay of migratory alpha-particle emitters. *Nuclear Instruments and Methods in Physics Research B*, **66**:379–387, 1992.
- [35] M. Kahn and A. L. Langhorst. A novel method for the preparation of carrier-free lead-212. *Journal of Inorganic Nuclear Chemistry*, **15**:384–389, 1960.
- [36] Boris Kayser. On the quantum mechanics of neutrino oscillation. *Physical Review D*, **24**(1):110–116, 1981.
- [37] Shripad M. Khopkar and Anil K. De. Cation-exchange studies of lead^{II} on dowex 50w-x8, separation from mixtures. *Talanta*, **7**:7–11, 1960.
- [38] I. M. Kolthoff and F. T. Eggertsen. Studies of aging and coprecipitation xxxiv the aging of freshly precipitated lead chromate. *Journal of the American Chemistry Society*, **63**:1412–1418, 1941.
- [39] A. E. Lally and K. M. Glover. Source preparation in alpha spectrometry. *Nuclear Instruments and Methods in Physics Research*, **223**:259–265, 1984.
- [40] K. Lande. Experimental results-homestake. In *Neutrino '94 conference*, 1994.
- [41] David R. Lide. *CRC Handbook of Chemistry and Physics*. CRC Press, 1980.
- [42] J. Liszi and Gy Bucsky. A new example for the applicability of the relationship between the particle size and the kinetic of the crystal growth. *Kristall und Technik*, **12**(8):781–788, 1977.

- [43] Manqing Liu, Henry W. Lee, and Art B. McDonald. ^{222}Rn emanation into vacuum. *Nuclear Instruments and Methods in Physics Research A*, **329**:291–298, 1993.
- [44] Harold M. Ide, William D. Moss, and Margaret A. Gautier. Bioassay α spectrometry: Energy resolution as a function of sample source preparation and counting geometry. *Health Physics*, **56**(1):71–77, 1989.
- [45] S. P. Mikheyev and A. Yu. Smirnov. Neutrino oscillations in a variable-density medium and ν -bursts due to the gravitational collapse of stars. *Soviet Physics - JETP*, **64**(1):4–7, 1986.
- [46] S. P. Mikheyev and A. Yu. Smirnov. Resonance enhancement of oscillations in matter and solar neutrino spectroscopy. *Sov. J. Nucl. Phys.*, **42**:913, 1986.
- [47] S. P. Mikheyev and A. Yu. Smirnov. Resonant amplification of ν oscillations in matter and solar-neutrino spectroscopy. *Nuovo Cimento*, **9C**(1):17–25, 1986.
- [48] John R. Moody and Richard M. Lindstrom. Selection and cleaning of plastic containers for storage of trace element samples. *Analytical Chemistry*, **49**(14):2264–2267, 1977.
- [49] Thomas J. Murphy. *National Bureau of Standards Special Publication 422*, 1976.
- [50] K. Nakamura. Recent results from kamiokande solar neutrino observations. *Nuclear Physics B*, **31**:105–110, 1993.
- [51] Nalgene. Nalgene company 1994 product catalog, 1994.
- [52] Bipin S. Parekh. *Reverse Osmosis Technology Applications for High-Purity-Water Production*. Marcel Dekker, Inc., 1988.
- [53] B. Pontecorvo. Neutrino experiments and the problem of conservation of leptonic charge. *Soviet Physics JETP*, **26**(5):984–988, 1968.

- [54] M. C. Rand, Arnold E. Greenberg, and Michael J. Taras. *Standard Methods For the Examination of Water and Wastewater*. American Public Health Association, American Water Works Association, Water Pollution Control Federation, fourteenth edition, 1975.
- [55] Michal Shatkay. Stripping of plated-out activities by various reagents - a preliminary report. Technical Report SNO-STR-95-001, Center for Research in Particle Physics, 1995.
- [56] Michal Shatkay, Ira Blevins, and Will Locke. Plate-out of ^{228}th , ^{224}ra and ^{212}pb onto pp, acrylic and hastelloy in upw and edta solutions. Technical Report SNO-STR-94-038, Center for Research in Particle Physics, 1994.
- [57] Michal Shatkay, D. Hazlett, David Sinclair, Cathy Shewchuk, A. Tweddle, and C. Striez. Measuring pb from large samples of aqueous solutions by use of reverse osmosis with the aid of edta. SNO Technical Report, in preparation.
- [58] Michal Shatkay, Cathy Shewchuk, David Sinclair, J. Hazlett, A. Tweddle, and C. Striez. The separation of lead on reverse osmosis and nano filtration membranes. Technical Report SNO-STR-92-093, Center for Research in Particle Physics, 1992.
- [59] Cathy Shewchuk, Michal Shatkay, and David Sinclair. Radium removal/monitoring in the sno experiment using mno_2 xad-7 resin. Technical Report SNO-STR-94-001, Center for Research in Particle Physics, 1994.
- [60] Claude W. Sill and Rodgers L. Williams. Preparation of actinides for α spectroscopy without electrodeposition. *Analytical Chemistry*, **53**:412-415, 1981.
- [61] Sylvaine Turck-Chièze, S. Cahen, and M. Casse. Revisiting the standard solar model. *The Astrophysical Journal*, **335**:415-424, 1988.

- [62] Sylvaine Turck-Chièze and Ilidio Lopes. Toward a unified classical model of the sun: On the sensitivity of neutrinos and helioseismology to the microscopic physics. *The Astrophysical Journal*, **408**:347–367, 1993.
- [63] V. S. Uras, P. Gérard, J. Tan, Henry W. Lee, and Art B. McDonald. Radon (^{222}Rn) emanation results. Technical Report SNO-STR-94-024, Center for Research in Particle Physics, 1994.
- [64] M. E. Vargas, J. D. Batchelor, and E. A. Schweikert. Trace determination of lead by helium-4 activation analysis. *Journal of Radioanalysis and Nuclear Chemistry Letters*, **119**(2):81–86, 1987.
- [65] Arthur Israel Vogel. *A Textbook of Quantitative Inorganic Analysis; including elementary instrumental analysis*. New York, Wiley, third edition, 1961.
- [66] G. J. Wasserburg, Fouad Tera, D. A. Papanastassiou, and J. C. Huneke. Isotopic and chemical investigations on angra dos reis. *Earth and Planetary Science Letters*, **35**:294–316, 1977.
- [67] L. Wolfenstein. Neutrino oscillations in matter. *Physical Review D*, **17**(9):2369–2374, 1978.
- [68] Jian xiong Wang, Tom Andersen, and John J. Simpson. Water radioactivity monitoring using electrostatic chamber. SNO technical report, 1993.
- [69] John Howe Yoe, Henry J. Hock, and Ralph E. Thiers. *Trace Analysis*, chapter 24. Wiley, New York, 1957.
- [70] Xian Zhu. Study of vacuum degassing for sno water system. Master's thesis, Queen's University, 1992.
- [71] Y. D. Zhugzhda and M. Stix. Acoustic waves in structured media and helioseismology. *Astronomy and Astrophysics*, **291**:310–319, 1994.

END

| 1 0 4 0 6 4 9 | 6

FIN