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STUDIES ON MATRIX INTERFERENCES AND MECHANISMS OF ATOMIZATION
OF CHROMIUM IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

© Bruno Marchand, M.Sc. (University of
Quebec in Rimouski)

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

Department of Chemistry
Carleton University
Ottawa, Ontario

August 1987

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~~Shaxrabadi~~

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ABSTRACT - The synthetic seawater matrix, which consists of NaCl, $MgCl_2$ and $CaCl_2$ causes severe chemical interferences in graphite furnace atomic absorption spectrometric determination of chromium VI and chromium III.

This thesis presents the results of the following studies made on the atomization of chromium: an empirical approach to mechanisms; the effects of different chloride matrices on the chromium atomic absorbance signal; an X-ray diffraction analysis; atomization from a dual-cavity graphite platform; a combined thermodynamic-kinetic approach to mechanisms.

Different activation energies related to different mechanisms of atomization for chromium VI in pure water and in synthetic seawater have been obtained using tube wall atomization and constant temperature atomization.

Finally, the atomization efficiency of a graphite probe furnace for chromium VI has been determined.

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INTRODUCTION

In the years after the demonstration of trivalent chromium as an essential trace element, a series of observations suggested that not only the valence state of the element but also its chemical environment determine metabolism and biological effects (1). The bioavailability of the element to the organism depends greatly on the chemical form of the species. For example, inorganic chromium is poorly utilized nutritionally, whereas an organic complex of chromium known as the glucose tolerance factor is highly utilized (1). Furthermore, present evidence suggests that the nutritionally important form of chromium which is contained in the difficult-to-analyze organic fraction is much more susceptible than inorganic chromium to matrix effects and loss during sample preparation (2). It may be inferred from the above studies that data on the biologically active fraction of chromium content in the aquatic environment may be more important than data on total chromium content.

The availability to organisms, and solubility in natural waters are among the factors which may be different for different chemical species of the same metal. In addition, the current interest in the various oxidation states of elements is mainly due to relatively recent evidence that the oxidation state may determine the toxicity of metal ions in the environment. For example, hexavalent chromium has higher toxicity than the trivalent form (3,4).

In the early stage of this research it was thought that

perhaps, graphite furnace atomic absorption spectrometry might provide a simple analytical technique for differentiating Cr (VI) from Cr (III) in pure water and in synthetic seawater. However, as will be seen later in this thesis, this proved not feasible because Cr (VI) and Cr (III) gave the same peak-height absorbance, presumably because Cr (VI) was rapidly converted into Cr (III) in the heated graphite furnace.

Chromium is a trace element present in various forms in natural waters depending on local redox, biological and solid phase conditions (5). Under normal oxidizing and pH conditions for seawater ($pE = 12.5$, $pH = 8.1$), the thermodynamically predicted state is Cr (VI) (as CrO_4^{2-}) (6). However, significant amounts of less soluble Cr (III) (as $Cr(OH)_3$) have also been found in natural oxygenated waters (7). Although, much of the reported oxidation state variation of chromium is undoubtedly a consequence of limitations of the various analytical methods used, it seems clear that redox equilibrium is not attained for the Cr (III) - Cr (VI) couple in seawater, and that in situ oxidation-reduction processes may be important controlling factors during the partitioning of chromium between soluble and particulate phases and, consequently, its removal from the water column (7).

Matrix interferences are considered to be a serious problem in graphite furnace atomic absorption spectrometry (GFAAS) (8-18). Matrix interferences can be classified into three categories: spectral, chemical and physical. Spectral interferences that are not caused

by an overlap of atomic lines can be eliminated in most cases by using the background correction technique. Chemical interferences may be caused by chemical reactions occurring either on the surface of the graphite furnace or in the vapour phase. Physical interferences are caused mainly by occlusion of the analyte in the matrix (18). In this work, matrix interferences with the determination of chromium VI in synthetic seawater by graphite furnace atomic absorption spectrometry have been studied.

Numerous workers have reported matrix interferences caused by chloride matrix in GFAAS. W. Slavin and D.C. Manning (19) have concluded that the chloride matrix causes great problems in the determination of lead. D.A. Segar and J.R. Gonzalez (20) have reported that copper is co-volatilized with sodium salts producing an attenuated signal for this element. J.A. Krasowski and T.R. Copeland (18) have studied the interference of various concentrations of NaCl, NaClO₄ and NH₄Cl on the atomic absorption signals of Cd, Cr, Cu and Pb and have found that the matrix concentrations up to 10 mg/mL cause less than 5% signal suppression in the constant-temperature furnace and up to 80% in the other atomizer used by them. G.R. Carnrick et al. (21) have reported that chloride matrix interferes in the determination of Mn in seawater. One of the objectives of this work is to determine and quantify the effects (enhancement or depression) of different chloride matrices on the chromium absorbance signal in GFAAS.

Several methods to overcome matrix interferences in GFAAS have been reported in the literature: standard addition method;

matrix-matched standard method; procedures involving separation of trace metals from salt matrix before atomization including extraction of trace metals as chelates (22-23); retention of the matrix by a column of hydrated antimony pentoxide (24); separation of the analyte by a column of ion-exchange resin (25); pre-concentration of trace metals on a hanging mercury drop (26); separation of trace elements by co-precipitation (27); removal of chloride ions by adding nitric acid (28-29); sodium peroxide (30) or ammonium nitrate (31). However, preconcentration and pretreatment procedures are not desirable in trace analysis since they may lead to contamination, loss, and change in the nature of analyte species, in addition to being laborious and slow. D.A. Segar and J.G. Gonzalez (20) have tried to overcome the matrix interference problem by using selective volatilization during the charring cycle. T. Nakahara and C.L. Chakrabarti (15) have reported that the selective volatilization technique is highly suitable for the determination of molybdenum in synthetic seawater. Others have reported successful application of matrix modifiers: EDTA (32), and ascorbic acid (33). Recently, new techniques such as the use of a constant-temperature furnace, and of pyrolytic graphite-coated tubes (34) have been reported. However, matrix interferences still remain an important problem, the solution of which requires understanding of the mechanisms of atomization and chemical reactions occurring in the graphite furnace.

Many approaches have been made in order to elucidate mechanisms of atom formation in graphite furnace: an empirical approach based

on the study of decomposition/atomization curves (35); a thermodynamic approach (36-37); a kinetic approach (38-39); a combined thermodynamic-kinetic approach (40). Also reported in the literature (41), is an evaluation of partial pressures of CO_2 , O_2 and CO gases present in the graphite furnace during atomization process as an aid to understanding of the mechanism of atomization in GFAAS. This thesis reports the results of the combined thermodynamic-kinetic approach using the method described in reference No. 42 for the determination of activation energy in a commercial, semi-enclosed graphite furnace using atomization from the tube wall, and also another method described in reference No. 43 for the determination of activation energy in a constant-temperature furnace using a graphite probe system.

Some workers have assumed thermodynamic equilibrium in a pulse-heated graphite furnace even though high thermal gradients, rapid rise in temperature and transient signals may not allow adequate time for physical and chemical processes to obtain an equilibrium state in the atomization process (41). However, pulse-heated graphite furnace atomizers offer the advantage of separating the drying, ashing and atomization processes. The atomization efficiency of such atomizers may depend on the composition of the matrix; also, such atomizers are not free of interferences.

Commercial electrothermal atomizers have two serious limitations in atomization from the tube wall: low heating rates limit them to much lower sensitivity than what is achievable at high heating rates (44-45); non-isothermal (spatial and temporal) conditions prevail in the furnace during most of the atomization cycle (46). Some

times the absorbance signal appears when the temperature of the furnace is rising in the atomization cycle; the sample is then vaporized and atomized from the hot central part of the graphite tube and a part of the vapour is condensed at the cold ends of the furnace resulting in a much lower residence time, and hence, in lower sensitivity and in memory effects (44). In a pulsed-heated graphite furnace, loss of analyte occurs by co-volatilization or carrier effect, when the species form molecular species in the vapour phase (16), by convection, or by diffusion.

The pulse-heated graphite furnace is a spatially and temporally dynamic system, inducing continuous change in the distribution of analyte within and between the condensed phase and the gas phase (47). In order to understand mechanisms of atomization, an empirical approach based on the study of decomposition/atomization curves for chromium VI and chromium III in pure water and in synthetic seawater has been also made in this work. The effects of different chloride matrices on the chromium signal have also been studied. Whether the atomization reactions occur in the condensed phase or in the vapour phase has been determined by using the dual-cavity graphite platform technique (48) reported by B. Welz. Also, a combined thermodynamic-kinetic approach has been proposed for the measurement and interpretation of activation energies for atom formation in the vapour phase. A physico-chemical method - X-ray diffraction - has been used to confirm the proposed mechanisms of atomization. The atomization efficiency of a graphite probe furnace for chromium VI in pure water and in synthetic seawater has also been determined.

CHAPTER 1

EXPERIMENTAL

1.1. APPARATUS

Three different commercial atomic absorption spectrophotometers were used for this research. Figure 1 shows a schematic diagram of a graphite furnace atomic absorption spectrophotometer.

A Perkin-Elmer atomic absorption spectrophotometer, model 503, modified to give fast response, was equipped with a deuterium-arc background corrector and a Perkin-Elmer HGA-2100 graphite furnace. A standard chromium hollow cathode lamp (Cathodeon Ltd.) was used. The absorbance and temperature were simultaneously recorded with a Nicolet model 4094, 4-channel, programmable digital oscilloscope, fitted with two plug-in units, model 4562, and an XF-44 disk recorder. Peak-area program and smoothing program were used in treatment of data. Signals were printed with a Hewlett-Packard, model 7470A graphics plotter.

The second atomic absorption spectrophotometer was a Perkin-Elmer, model 5000, equipped with a Zeeman background correction system and a Perkin-Elmer HGA-500 graphite furnace. Absorbance signals (peak-height and peak-area) were recorded with a Perkin-Elmer, model 7500 professional computer, using HGA Graphics IX, and were printed with a model 132 printer (Integral Data Systems).

Figure 1. Schematic diagram of a graphite furnace atomic absorption spectrophotometer.

Figure 2. Schematic diagram of the probe apparatus.

1. Graphite probe
2. Probe holder
3. Cylinder shaft
4. Stop
5. Slide guide (fixed to the cylinder shaft)
6. Adjustable support rods
7. Air flow control valve

Graphite probe experiments were done with a Perkin-Elmer atomic absorption spectrophotometer, model 5000, equipped with a deuterium-arc background corrector for the UV range and a tungsten iodide lamp for the visible range. The graphite furnace was a Perkin-Elmer PGA-500. A graphite probe system (described in Fig. 2 and in reference 49) was used with the instrument. The sample injection port of the Perkin-Elmer pyrocoated graphite tube was enlarged to give a rectangular slot of 1.8 mm in height and 4.5 mm in width along the tube length. The left contact electrode of the graphite furnace was modified to allow insertion of the graphite probe in the graphite tube. The probe was mounted on a ceramic holder which was fixed on the shaft of a two-way air cylinder (49). The displacement of the cylinder was controlled by a 4-way, laboratory made, solenoid power supply controller (Fig. 2) (49). Absorbance signals were recorded and printed in the same way as was done with the previous spectrophotometer. A Perkin-Elmer computer program was used to get the absorbance values as a function of time - a reading being taken every 17 ms.

X-ray diffraction analysis was done with a Philips automated powder diffractometer, PW 1050/81, equipped with a PW 1710 micro-processor. Monochromated Cu radiation at a voltage of 40 kV and a current of 40 mA was used.

1.2. GRAPHITE TUBES, PLATFORMS AND PROBES

The Perkin-Elmer pyrolytically - coated graphite tubes were used

for all experiments. The Perkin-Elmer pyrocoated graphite tubes with grooves inside were used for the dual-cavity experiments. Graphite platforms with two cavities were fabricated in-house from blocks of pyrolytic graphite. The rectangular slot of graphite tubes was enlarged (20 mm x 4 mm) to allow injection of samples into cavities of the platform with a micropipet.

The trapezoidal graphite probes were made of a block of anisotropic pyrolytic graphite. The dimensions of probes were approximately 25 mm long and 4 mm wide at the head, 2 mm wide at the other end, and its thickness was from 0.18 mm to 0.48 mm. The Perkin-Elmer pyrolytically-coated graphite platforms were used for X-ray diffraction analysis.

1.3. MEASUREMENT OF THE TEMPERATURE

1.3.1. ATOMIC ABSORPTION SPECTROPHOTOMETERS, MODEL 503 AND 5000 (ZEEMAN).

The inside tube wall temperature was measured directly below the sample injection hole with two automatic optical pyrometers (Ircon inc., Skokie, Illinois, USA). The optical pyrometer, series 300, was used for low temperatures ($<900^{\circ}\text{C}$) and the optical pyrometer, series 1100, for high temperatures ($>900^{\circ}\text{C}$). The temperature profiles, recorded in millivolts by the oscilloscope, were converted into degree Celsius, using calibration curves obtained by calibrating the optical pyrometer against a black-body.

1.3.2. ATOMIC ABSORPTION SPECTROPHOTOMETER, MODEL 5000, WITH THE PROBE SYSTEM.

Three different temperatures of the graphite probe furnace were measured. The outside tube wall temperature was measured with the automatic optical pyrometer, series 1100, and recorded with the Nicolet oscilloscope. The effective (steady-state) gas temperature was determined by the two-line atomic absorption method using Sn 286.3/284.0 nm line pair (50,51). Finally, the probe surface temperature in the graphite furnace was determined using the computer program described in reference 78.

1.4. REAGENTS

A stock solution containing 1000 $\mu\text{g/mL}$ of chromium was prepared by dissolving the appropriate mass of potassium dichromate, Fisher Certified Reagent (99.98% pure), in 1% (v/v) ULTREX nitric acid/aqueous solution, and making up to 1 liter with ultrapure water. Ultrapure water with a resistivity of 18.3 megohms-cm was obtained direct from a Milli-Q2 water purification system (Millipore Corporation). All glasswares were washed with 50% (v/v) nitric acid reagent grade for two weeks and with 20% (v/v) nitric acid (reagent grade) for a further two weeks. Synthetic seawater having the three major chloride salts (NaCl , MgCl_2 and CaCl_2) in the proportion they exist in seawater, with a salinity of 35 parts per thousand (Table 1), was pre-

pared using the following reagents: sodium chloride (analytical reagent grade, BDH) 99.9% pure, magnesium chloride (Baker Analyzed Reagent, J.T. Baker Chemical Co.), 99.4% pure, and calcium chloride (Certified A.C.S. Reagent), Fisher Scientific Co.), 95.8% pure.

Table 1. Synthetic seawater composition (J. Lyman and R. Fleming (53))

(g/L)			
NaCl	23.939	KBr	0.098
MgCl ₂	5.079	H ₃ BO ₃	0.027
Na ₂ SO ₄	3.994	SrCl ₂	0.024
CaCl ₂	1.123	NaF	0.003
KCl	0.667	NaHCO ₃	0.196

1.5. GAS

High-purity argon gas (99.995% pure, Union Carbide Ltd.) was used as purge and sheath gas for the graphite furnace.

1.6. GENERAL PROCEDURES

1.6.1. ATOMIC-ABSORPTION-SPECTROPHOTOMETRIC MEASUREMENT

Test solutions of chromium VI and chromium III were prepared by serial dilutions of the stock solution with ultrapure water. To reduce the hexavalent chromium to trivalent chromium, 1% (v/v) Ultrex nitric acid/aqueous solution and few drops of 30% hydrogen peroxide were added to the solution of chromium VI. After one hour, the solution was heated to removed the excess hydrogen peroxide and the cooled solution was then diluted with ultrapure water up to the mark (54).

1.6.2. X-RAY DIFFRACTION ANALYSIS

For the X-ray diffraction analysis, an aqueous solution containing 240 μg of chromium in pure water or in synthetic seawater (diluted ten-fold) were used. The solutions were deposited on graphite platforms with a 20 μL micropipet, and were dried by placing platforms under an infrared lamp. Platforms containing the sample were then heated in the graphite furnace using the pre-determined times and the atomic absorption spectrophotometer, model 503. After,

graphite platforms were cooled to room temperature inside the furnace and they were taken out and subjected to X-ray diffraction analysis. The X-ray diffraction spectra obtained were compared with the standard X-ray diffraction data (55) to identify the species present in the condensed phase.

1.7. EXPERIMENTAL CONDITIONS

The experimental and operating conditions used are summarized in Tables 2, 3 and 4. Table 5 shows the experimental conditions for the atomic absorption spectrophotometer, model 503, used to prepare the pre-atomization residues, for X-ray diffraction analysis. Table 6 shows the experimental conditions used for the X-ray diffractometer for X-ray diffraction analysis.

Table 2. Experimental and operating conditions for the Perkin-Elmer atomic absorption spectrophotometer, model 503.

PARAMETERS	CHROMIUM IN PURE WATER	CHROMIUM IN SYNTHETIC SEA- WATER
MASS (kg)	2.5×10^{-11}	2.5×10^{-11}
WAVELENGTH (nm)	357.9	357.9
SLIT WIDTH (nm)	0.7	0.7
LAMP CURRENT (mA)	6	6
DRYING TEMPERATURE ($^{\circ}\text{C}$)	100	100
TIME (s)	120	120
CHARRING TEMPERATURE ($^{\circ}\text{C}$)	900	1100
TIME (s)	24	24
ATOMIZATION TEMPERATURE ($^{\circ}\text{C}$)	2600	2600
TIME (s)	5	5
ARGON FLOW RATE (L/min)	INTERRUPT-MODE 0.3	INTERRUPT-MODE 0.3
MANUAL INJECTION (μL)	5	5

• IN-ATOMIZATION STEP

Table 3. Experimental and operating conditions for the Perkin-Elmer Zeeman atomic absorption spectrophotometer, model 5000.

PARAMETERS	CHROMIUM IN PURE WATER	CHROMIUM IN SALT MATRIX
MASS (kg)	2.5×10^{-11}	2×10^{-11}
WAVELENGTH (nm)	357.9	357.9
SLIT WIDTH (nm)	0.7	0.7
LAMP CURRENT (mA)	10	10
DRYING TEMPERATURE (°C)	100	110
RAMP TIME (s)	60	60
HOLD TIME (s)	20	20
CHARRING TEMPERATURE (°C)	900	1100
RAMP TIME (s)	20	20
HOLD TIME (s)	20	20
COOLING TEMPERATURE (°C)	20	20
RAMP TIME (s)	5	5
HOLD TIME (s)	5	5
ATOMIZATION TEMPERATURE (°C)	2600	2600
RAMP TIME (s)	0	0
HOLD TIME (s)	6	6
CLEANING TEMPERATURE (°C)	2700	2700
RAMP TIME (s)	1	1
HOLD TIME (s)	5	5
COOLING TEMPERATURE (°C)	20	20
RAMP TIME (s)	1	1
HOLD TIME (s)	5	5
ARGON FLOW RATE (L/min)	INTERRUPT-MODE** 0.3	INTERRUPT-MODE** 0.3
MANUAL INJECTION (μL)	5	5

* FOR GRAPHITE PLATFORMS
 ** IN ATOMIZATION STEP

Table 4. Experimental and operating conditions for the Perkin-Elmer atomic absorption spectrophotometer, model 5000, fitted with the graphite probe furnace.

PARAMETERS	CHROMIUM VI IN PURE WATER	CHROMIUM VI IN SYNTHETIC SEAWATER
MASS (kg)	2.5×10^{-11}	2.5×10^{-11}
WAVELENGTH (nm)	357.9	357.9
SPLIT (nm)	0.7	0.7
LAMP CURRENT (mA)	10	10
DRYING TEMPERATURE ($^{\circ}\text{C}$)	100	110
RAMP TIME (s)	20	20
HOLD TIME (s)	60	60
COOLING TEMPERATURE ($^{\circ}\text{C}$)	20	20
RAMP TIME (s)	5	5
HOLD TIME (s)	5	5
ATOMIZATION TEMPERATURE ($^{\circ}\text{C}$)	2600	2600
RAMP TIME (s)	0	0
HOLD TIME (s)	6	6
CLEANING TEMPERATURE ($^{\circ}\text{C}$)	2700	2700
RAMP TIME (s)	1	1
HOLD TIME (s)	5	5
COOLING TEMPERATURE ($^{\circ}\text{C}$)	20	20
RAMP TIME (s)	5	5
HOLD TIME (s)	5	5
ARGON FLOW RATE (L/min)	INTERRUPT-MODE [*] 0.3	INTERRUPT-MODE [*] 0.3
INSERTION TIME FOR PROBES (s)	3	3
MANUAL INJECTION (μL)	5	5

* IN ATOMIZATION STEP

Table 5. Experimental conditions for the atomic absorption spectrophotometer, model 503, used to prepare the pre-atomization residues, for X-ray diffraction analysis.

PARAMETERS	CHROMIUM VI IN PURE WATER	CHROMIUM VI IN SYNTHETIC SEAWATER
PRE-ATOMIZATION TEMPERATURE (°C)	1000	1100-1200* -1300 1400-1500-1600
PRE-ATOMIZATION TIME (s)	45	45

* PRE-ATOMIZATION TIME: 45 AND 90 SECONDS

Table 6. Experimental conditions used for the diffractometer
for X-ray diffraction analysis.

RADIATION TYPE	COPPER, K
WAVELENGTH (Å)	1.5418
CURRENT (mA)	30
VOLTAGE (kV)	40
EXPOSURE TIME (hr)	4
MASS OF CHROMIUM VI (μg)	240

$$F \text{ (atoms/cm}^2 \text{ s)} = f(A_1 T \cdot S) \quad 7$$

The time-dependent variation of $N(t)$ can be expressed as a convolution integral (64):

$$N(t) = \int_0^t S(t') R(t-t') dt' \quad 8$$

where $S(t) = (dN/dt)_{in}$ is the supply rate of atoms and $R(t)$ is the normalized response of the system ($R_{max} = 1$) upon the supply of an infinitely rapid pulse of atoms.

Information on the energetics of sample vaporization can be obtained from the supply function. There is a first-order dependence on the mass of analyte present on the atomizer surface:

$$S(t) = \left[\frac{dN}{dt} \right]_{in} = \frac{dN_w}{dT} = B \exp [-E_a/RT(t)] N_w \quad 9$$

where

N_w = the number of analyte atoms on the atomizer surface

B = frequency factor

E_a = activation energy

Figure 3. Typical absorbance pulse characterization times.

where

A = pre-exponential factor

E_a = activation energy for atom formation

k = the Boltzmann constant

T = absolute temperature

The effective length of the absorbing layer of atoms along the furnace axis (assuming uniform distribution of analyte atoms across the cross-section, S, of the furnace) at any time, t, is related to the number of atoms in the tube, $N_{(t)}$, by the following expression (58):

$$\int_0^l n(x, t) dx = \frac{N_{(t)}}{S} \quad 2$$

where l is the furnace length.

Assuming that the concentration gradient of atoms along the furnace from the middle point to the ends is constant, the mean residence time (τ_2) of analyte atoms in the furnace is related to the coefficient of diffusion of the analyte atoms as follows (58):

$$\tau_2 = \frac{l^2}{8 D} \quad 3$$

where D is the coefficient of diffusion.

Analysis of the transport process of the sample through the analysis volume shows that the integrated value (Q_N) of the number of absorbing atoms can be expressed through the total number of atoms of the analyte introduced into the analysis cell (N_0) and the residence time (τ_2) of atoms (58).

$$Q_N = \int_0^{\infty} N(t) dt = N_0 \tau_2 \quad 4$$

Substituting equation 4 into equation 2 for the integral value of the analytical signal, Q_{nl} , expressed in the units of the effective length of the absorbing layer and by using equation 3, equation 4 can be written as (58)

$$Q_{nl} = \frac{l^2}{8 D S} N_0 \quad 5$$

Equations 4 and 5 show that the integrated signal (peak-area) is independent of τ_1 , and hence, of kinetics of atom formation. Therefore, the integrated signal is independent of the sample composition, and is therefore preferable to the peak-height method. The latter is sensitive to kinetics of atom formation. However, as equation 4 shows, the integration method requires fulfilment of two conditions: the constancy of N_0 (i.e., the sample must be completely atomized) and of τ_2 (i.e., the residence time must be held constant). For the correct application of the integration method, the experimental conditions must be such as to fulfil the above-mentioned two conditions.

exists within the furnace and the production of observable atoms is characterized by a first-order rate constant. Consecutive, first-order reactions that occur in an anisotropic pyrolytic graphite tube atomizer at a constant temperature may be described as follows (43).

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where

A = the pre-atomization analyte species

B = the absorbing analyte atoms that are formed

C = the analyte atoms that are lost from the

analysis volume

k_1 = first-order rate constant for atom formation

k_2 = first-order rate constant for atom loss

Elucidation of the detailed mechanism of atomization usually starts with a determination of the activation energy (E_a) which characterizes the rate-determining step. The most widely used method of obtaining mechanistic information is from a kinetic analysis of the temporal variation in the atomic absorption signal.

For negligible condensation, the flux of analyte atoms (F) vaporizing from a surface defines the rate of the reaction and is experimentally a function of the surface concentrations of reacting species in the rate limiting reaction step (A_1), the absolute temperature (T) and the surface area of the vaporizing material (S), and their relationship is expressed by equation 7.

$$F \text{ (atoms/cm}^2 \text{ s)} = f(A_i T \cdot S)$$

7

The time-dependent variation of $N(t)$ can be expressed as a convolution integral (64):

$$N(t) = \int_0^t S(t') R(t-t') dt' \quad 8$$

where $S(t) = (dN/dt)_{in}$ is the supply rate of atoms and $R(t)$ is the normalized response of the system ($R_{max} = 1$) upon the supply of an infinitely rapid pulse of atoms.

Information on the energetics of sample vaporization can be obtained from the supply function. There is a first-order dependence on the mass of analyte present on the atomizer surface:

$$S(t) = \left[\frac{dN}{dt} \right]_{in} = \frac{dN_w}{dT} = B \exp [-E_a/RT(t)] N_w \quad 9$$

where

N_w = the number of analyte atoms on the atomizer surface

B = frequency factor

E_a = activation energy

If

$$N_o = \int_0^{\infty} S(t) dt = N_w(t=0) \quad 10$$

then

$$S(t) = B \exp [-E_a/RT_{(t)}] N_o \exp \left[- \int_0^t B \exp [-E_a/RT_{(t')}] dt' \right] \quad 11$$

The amount of material left on the tube surface is given by:

$$\int_t^{\infty} S(t) dt = N_o \exp \left[- \int_0^t B \exp [-E_a/RT] dt \right] \quad 12$$

To obtain an expression for the rate constant (k_1), Smets (42) normalized the $S(t)$ function by dividing equation 11 by the expression 12:

$$k_1 = \frac{S(t)}{\int_t^{\infty} S(t) dt} \propto \frac{A(t)}{\int_t^{\infty} A(t) dt} \propto B \exp [-E_a/RT_{(t)}] \quad 13$$

where A is the measured absorbance.

Equation 13 is used to obtain activation energies from absorbance signals. The rate constant, k_1 , is determined from the experimental atomic absorption pulse (absorbance as a function of time), and k_1 is evaluated using equation 13. The natural logarithm of k_1 is plotted against the reciprocal of temperature. This method

(42) was used when the atomization occurred under non-isothermal conditions, such as, in atomization from the atomizer tube wall.

For atomization at constant temperature in a graphite furnace atomic absorption spectrometry, the method used by C.L. Chakrabarti et al. (43) was employed. If k_1 and k_2 are first-order rate constants for atom formation and atom loss, respectively, then from equation 6, one can obtain equation 14:

$$[A]_t + [B]_t + [C]_t = [A]_0 \quad 14$$

where

[] = concentrations of species shown inside the brackets

t = time

$[A]_0$ = the concentration of [A] at time = 0, i.e., the initial concentration of A

Assuming first-order kinetics, the following differential equations can be written from equation 6:

$$\frac{d[A]}{dt} = -k_1[A] \quad 15$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad 16$$

In the limits, [A] tends to zero (exhaustion of the supply of the pre-atomization species A). Then, equation 16 becomes:

$$\frac{d[B]}{dt} = -k_2[B]$$

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By using the absorbance signal as a function of time, plots of the natural logarithm of absorbance vs time were drawn. The rate constant for atom loss, k_2 , was then determined from the slope of the decay part of the absorbance signal using only those data points towards the end of the absorption pulse where loss of analyte atoms by diffusion was the only process occurring. Extrapolation of this slope to the time 0 of the absorption pulse gave the initial concentration of B. The difference between the extrapolated absorbance and the experimental absorbance at any time (t) in the rising part of the signal was due to the concentration of the pre-atomization species A. The slope was therefore equal to the rate constant for atom formation, k_1 . The natural logarithm of the rate constant vs the reciprocal of absolute temperature was then plotted (the Arrhenius plot). The activation energy was determined from the slope of the linear Arrhenius plot.

To elucidate mechanisms of atomization that occur in the graphite furnace, the experimental activation energies obtained by using the above two different methods were compared with the theoretical ΔH^θ for various possible reaction sequences. Because the reactions are highly endothermic it is reasonable to treat $E_a \approx \Delta H^\theta$.

2.3. ATOMIZATION EFFICIENCY

Following the treatment given earlier by C.L. Chakrabarti et al. (43), the efficiency of an HGA-500 graphite furnace for production and containment of atomic vapour (66) has been determined using the graphite probe technique (isothermal atomization) for chromium VI in pure water and in synthetic seawater. Two different atomization efficiencies, β_1 and β_2 , have been calculated from the experimental data. Both β_1 and β_2 give the fraction of analyte which is present as atomic vapour at the peak of the absorbance signal profile.

In order to simplify the treatment, other chemical reactions such as ionization, adsorption on the graphite surface, formation of refractory compounds, etc., and physical processes are ignored; only the transport of analyte atoms in the analysis volume (defined by the geometry of the incident beam of radiation from the hollow-cathode lamp) is considered. It is assumed that the chromium is in the atomic state in the graphite furnace and that the conversion of D into B, and that of B into C are consecutive, first-order reactions.

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where

D = the pre-atomization analyte species

B = the absorbing analyte atoms

C = the analyte atoms that are lost from the analysis volume

The model yields the differential equations 19 and 21.

$$\frac{d[D]}{dt} = -k_1 [D] \quad 19$$

Solution of equation 19 is given by equation 20:

$$[D] = [D]_0 \exp(-k_1 t) \quad 20$$

$$\frac{d[B]}{dt} = k_1 [D] - k_2 [B] \quad 21$$

Solution of equation 21 is obtained using the solution of equation 19, where the initial concentration of the species D is $[D]_0$ and with no B present initially:

$$[B]_t = \frac{[D]_0 k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) \quad 22$$

where $[B]_t = [B]$ at time t , where the bracket $[]$ denotes the concentration of the species inside the bracket.

$[B]_t$ is related to the measured absorbance (A) by using a factor p , where B is a constant relating measured absorbance to the amount of analyte atoms in the analysis cell.

$$A = p \frac{[D]_0 k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) \quad 23$$

The concentration of the pre-atomization species D decreases with time. The concentration of B, which is initially zero, at first increases, reaches a maximum when $d[B]/dt = 0$. By differentiating equation 22, the expression for the time $t_{\max}$ required for the attainment of the absorbance maximum ($d[B]/dt = 0$) can be obtained:

$$k_1 \exp(-k_1 t_{\max}) = k_2 \exp(-k_2 t_{\max}) \quad 24$$

or,

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad 25$$

The maximum concentration of B is then:

$$[B]_{t_{\max}} = [D]_0 \exp(-k_2 t_{\max}) \quad 26$$

The efficiency of atomization β_1 is defined as the fraction of analyte present as atomic vapour at $t_{\max}$:

$$\beta_1 = \frac{[B]_{t_{\max}}}{[D]_0} = \exp(-k_2 t_{\max}) \quad 27$$

An alternative method can be derived from the definition of β_1 , yielding another atomization efficiency, to be called β_2 . The atomization efficiency, β_2 , is defined as the maximum number of atoms, $N_{\max}$, present as atomic vapour at ($t_{\max}$) over the total number of atoms present initially, N_0 (Fig. 4):

$$\beta_2 = \frac{N_{\max}}{N_0} = \frac{A_{\max}}{A_0} \quad 28$$

where

$A_{\max}$ = the maximum in the absorbance signal, as defined by Fig. 4.

By definition, β_1 should be equal to β_2 .

For the calculation of β_1 , the absorbance signal must be obtained under isothermal conditions because k_2 is dependent on the temperature. Introduction of a graphite probe containing the analyte species into the graphite furnace immediately prior to the atomization cycle of the graphite furnace results in atomization under isothermal conditions. (43,66).

From the equation 27, β_1 will be approximatively equal to 1 if $k_2 t_{\max} \ll 1$. Hence, for the highest atomization efficiency, k_2 and $t_{\max}$ must be as small as possible. Since the rate constant k_2 increases with increasing atomization temperature, and high heating rates give small $t_{\max}$ values, maximum atomization efficiency should occur at moderately high atomization temperatures coupled with high heating rates.

Figure 4. Typical plot of peak-height absorbance vs time.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. THERMAL DECOMPOSITION (CHARRING)-ATOMIZATION CURVES FOR CHROMIUM III AND CHROMIUM VI IN PURE WATER AND IN SYNTHETIC SEAWATER.

Figures 5 - 9 show decomposition curves and atomization curves of chromium III and chromium VI atomized from pyrocoated graphite tubes walls of the graphite furnace. The left-hand curve (decomposition curve) is a plot of chromium absorbance at a constant, optimum atomization temperature as a function of charring temperature. The optimum charring temperature is considered to be the temperature which is arbitrarily set at about 100°C lower than the maximum temperature of the plateau region of the charring curve (i.e., before the curve starts to descend because of loss of chromium atoms). The right-hand curve (atomization curve) is a plot of chromium absorbance at the constant, optimum charring temperature as a function of atomization temperature. Each point in the curves represents the mean value of at least two determinations.

Figure 5 shows that the decomposition (charring)-atomization curves for chromium VI coincide with those of chromium III in pure water for atomization from the tube wall. Probably, chromium VI is rapidly reduced to chromium III in the reducing environment of the heated graphite furnace. It was therefore decided that only chromium VI would be studied further.

The left-hand curve (decomposition curve) of Fig. 5 shows that the peak height absorbance for both chromium VI and chromium III remains constant with increasing charring temperature from 400 °C to 1200 °C. Above 1200 °C, the absorbance of chromium decreases rapidly, indicating a pre-atomization loss of some chromium atoms from the furnace. The right-hand curve (atomization curve) shows a continuous increase in the peak-height absorbance with increasing atomization temperature until the absorbance reaches a maximum at 2600 °C. The appearance temperature, which is defined as the temperature at which the signal of chromium atom just becomes distinguishable from the baseline signal is about 1400 °C.

Figure 6 shows the decomposition-atomization curves for chromium VI in pure water and in synthetic seawater obtained by atomization from the tube wall using the Zeeman atomic absorption spectrophotometer, model 5000. The curve with circles represents chromium VI in pure water and that with triangles represents chromium VI in synthetic seawater. The left-hand curve shows that the peak-height remains constant at about 0.25 absorbance from 400 °C to 1000 °C. Above that temperature, thermal decomposition and pre-atomization loss of chromium occurs. The absorbance decreases as a function of increasing decomposition temperature. The right-hand curve shows that the appearance temperature was about 1400 °C and the peak-height absorbance increases sharply with increasing atomization temperature until the plateau region starts at 1500 °C. The optimum atomization temperature used was 2600 °C. The appearance temperature for chromium VI in pure water

was about 1400°C (1670 K) compared with that for chromium in synthetic seawater, about 1720°C (1990 K). Sturgeon et al. (50) have found that the same atomization mechanism of an analyte element results in the same appearance temperature regardless of the chemical form (species) of the analyte element which is undergoing atomization. The above observation would suggest a different mechanism of atomization for chromium VI in pure water from that in synthetic seawater. Table 7 shows the appearance temperature of chromium VI in pure water and in synthetic seawater compared with the appearance temperature of chromium VI in pure water reported by R.E. Sturgeon et al. (49).

Table 7. Appearance temperature of chromium VI.

ANALYTE ELEMENT IN MATRIX	APPEARANCE TEMPERATURE (K)
Cr VI IN PURE WATER	1670
Cr VI IN SYNTHETIC SEAWATER	1990
Cr VI IN PURE WATER*	1660

* REF 49

The decomposition-atomization curves for chromium VI in synthetic seawater show approximately the same behaviour as those for chromium VI in pure water. The optimum charring temperature increased to 1100°C , but the optimum atomization temperature was the same (2600°C) as that for chromium VI in pure water. However, the peak-height absorbance showed an enhancement of about 45% for both the decomposition and atomization curves. By using the same kind of curves for molybdenum in a salt matrix, T. Nakahara and C. L. Chakrabarti (15) have concluded that the presence of NaCl , Na_2SO_4 and KCl causes a decrease in the molybdenum signal, and that of MgCl_2 and CaCl_2 a pronounced enhancement.

In the following chapter, the effects of different chloride matrices on the absorbance signal for chromium VI will be studied in greater depth.

Figure 7 shows the thermal decomposition-atomization curves drawn using integrated absorbance (peak-area) for chromium VI in pure water and in synthetic seawater. The experimental and operating conditions were the same as for the curves drawn using peak-height absorbance. The shapes of both of these curves are very similar. The same behaviour was observed for chromium VI in pure water and in synthetic seawater. Integrated peak absorbance signals are commonly used to determine quantitatively the analyte since change in the peak-height caused by the matrix does not affect peak-area absorbance (63). The peak-height absorbance is a function of the rate at which the atoms enter and leave the analysis volume whereas the area under the peak is a function of only the rate at which the atoms leave the analysis volume (18, 39).

Figures 8 and 9 show thermal decomposition-atomization curves for chromium III in pure water and in synthetic seawater drawn using peak-height absorbance and peak-area absorbance, respectively. The curves have shapes very similar to those curves for chromium VI. This is consistent with the earlier observation that chromium VI and chromium III have the same analytical sensitivity.

Figure 5. Decomposition-atomization curves for chromium VI and chromium III obtained using the atomic absorption spectrophotometer, model 503. ● thermal decomposition (charring) curve for chromium III in pure water, ■ thermal decomposition (charring) curve for chromium VI in pure water, ○ thermal atomization curve for chromium III in pure water, □ thermal atomization curve for chromium VI in pure water.

Figure 6. Decomposition-atomization curves for chromium VI obtained using the Zeeman atomic absorption spectrophotometer, model 5000. ● thermal decomposition (charring) curve for chromium VI in pure water, ▲ thermal decomposition (charring) curve for chromium VI in synthetic seawater, ○ thermal atomization curve for chromium VI in pure water, △ thermal atomization curve for chromium VI in synthetic seawater.

Figure 7. Decomposition-atomization curves for chromium VI obtained using the Zeeman atomic absorption spectrophotometer, model 5000. ● thermal decomposition (charring) curve for chromium VI in pure water, ▲ thermal decomposition (charring) curve for chromium VI in synthetic seawater, ○ thermal atomization curve for chromium VI in pure water, △ thermal atomization curve for chromium VI in synthetic seawater.

Figure 8. Decomposition-atomization curves for chromium III obtained using the Zeeman atomic absorption spectrophotometer, model 5000. ● thermal decomposition (charring) curve for chromium III in pure water, ▲ thermal decomposition (charring) curve for chromium III in synthetic seawater, ○ thermal atomization curve for chromium III in pure water, △ thermal atomization curve for chromium III in synthetic seawater.

Figure 9. Decomposition-atomization curves for chromium III obtained using the Zeeman atomic absorption spectrophotometer, model 5000. ● thermal decomposition (charring) curve for chromium III in pure water, ▲ thermal decomposition (charring) curve for chromium III in synthetic seawater, ○ thermal atomization curve for chromium III in pure water, △ thermal atomization curve for chromium III in synthetic seawater.

3.2. EFFECTS OF DIFFERENT CHLORIDE MATRICES ON THE CHROMIUM ABSORBANCE SIGNAL AND ON THE ABSORBANCE PULSE CHARACTERIZATION TIMES.

Figure 10 and 11 show the effects of different chloride matrices (synthetic seawater, NaCl , MgCl_2 , or CaCl_2) on the absorbance pulse of chromium VI in an aqueous solution. The peak-height absorbance of chromium VI in synthetic seawater was much greater than that of chromium VI in pure water.

Table 8 shows the effects of different chloride matrices on the peak-height and the peak-area absorbance of Cr (VI) atomized from the tube wall. The peak-height absorbance of Cr (VI) suffered serious matrix interference from the chloride matrices, whereas the peak-area absorbance was unaffected by the matrices. It was therefore reasonable to conclude that the matrix interference with the peak-height absorbance was due to change in the rate of atomization of chromium from different matrices. It was decided to study the origin of the interference - whether it was condensed-phase or vapour-phase interference. In order to understand the nature of the matrix interference it was also decided to study the mechanisms of chromium atom formation and dissipation when Cr (VI) was present in aqueous solution in the presence or absence of the chloride matrices. This was done in the following chapters.

White fumes were observed to emanate from the sample injection hole when chromium VI in a NaCl matrix (in an aqueous solution) was

heated in the charring cycle. Because of this expulsion of NaCl fumes through the sample injection hole, a partial loss of chromium by expulsion through the sample injection hole probably occurred in the charring cycle (20). Such a loss of chromium might be the result of a part of the chromium existing as gaseous chloride, $\text{CrCl}_3(\text{g})$ in the charring cycle. B.V. L'vov (58) has suggested that part of some analyte element is bound with halide in the vapour phase. J.A. Krasowski and T.R. Copeland (18) have proposed that the analyte is trapped (occluded) within the crystals of the dried matrix in the furnace and some of the crystals are mechanically expelled from the furnace with the expanding gases. However, occlusion is an unlikely explanation for halide interferences (59).

When an analyte is present in a high concentration of a volatile matrix (e.g. NaCl), a partial loss of the gaseous analyte species by expulsion with the expanding gases of the matrix (e.g. NaCl) that occurs through the injection hole, is known as the carrier effect (60). Also, at the end of the atomization cycle, the ends of the graphite tube and cones of the furnace were found to be coated with a layer of salt, probably resulting from condensation of the analyte with the matrix. It should be noted that the vaporization of the sodium chloride matrix occurs at about 900-1000 °C. Another fact which supports the carrier effect was that the appearance time of the absorbance signal for chromium VI in NaCl (aqueous solution) occurred earlier than that of chromium VI in pure water. This suggests that the loss of the analyte in graphite furnace atomic absorption spectrometry

Figure 10. Effects of different chloride matrices on the chromium VI

signal.

Figure 11. Effects of synthetic seawater matrix on the chromium VI signal.

might be partly due to convection and diffusion of Cr atoms through the sample injection hole and porous walls of the furnace (13) or expulsion of the sample vapour through the sample injection hole (61).

For MgCl_2 , CaCl_2 , or synthetic seawater, no white fumes were observed during the charring cycle at the optimum charring temperature used, probably because the boiling points of MgCl_2 and CaCl_2 were higher than the highest charring temperature used.

Because the peak-area of chromium signals in different matrices have nearly the same value, the residence time (τ_2) which is given by the equation : $Q = N \cdot \tau_2$ should be nearly the same (51).

Table 9 shows the characterization times of the absorbance pulses for chromium VI in the different matrices. The Perkin-Elmer Zeeman atomic absorption spectrophotometer and atomization from the tube wall were used. Table 9 shows that the τ_{app} , τ_1 and τ_2 for chromium VI in synthetic seawater are lower than those for chromium VI in pure water. The lower values of τ_{app} and τ_1 indicate that the rate of $\text{Cr}_{(\text{g})}$ formation (which is inversely proportional to the time for a first-order process) from synthetic seawater is greater than that from pure water. The lower value of τ_2 may be due to loss of gaseous Cr-species by expulsion along with the expanding vapour of the matrix molecular species through the sample injection hole and / or due to loss by condensation at the cooler ends of the graphite tube along with the NaCl condensate. The τ_1 / τ_2 ratios range from 0.66 to 0.31, which are much larger than the ratio (< 0.1) required for satisfactory application of the peak-height mode of measurement (51). Since,

the peak-area of chromium signals in different matrices have nearly the same value, the peak-area mode of measurement is preferred to the peak-height mode for chromium in the above matrices.

Table 8. Effects of different chloride matrices on the peak-height and the peak-area absorbance of 1.5×10^{-13} kg of chromium VI with the Zeeman atomic absorption spectrophotometer, model 5000, and atomization from tube wall.

	Cr VI IN PURE WATER	Cr VI IN SYN- THETIC SEAWATER	Cr VI IN NaCl AQUEOUS SOLUTION	Cr VI IN MgCl ₂ AQUEOUS SOLUTION	Cr VI IN CaCl ₂ AQUEOUS SOLUTION
PEAK- HEIGHT ABSORBANCE	0.288	0.568	0.260	0.420	0.347
PEAK- AREA ABSORBANCE	0.189	0.174	0.179	0.201	0.206

Table 9. Characterization times of the absorbance pulses for chromium VI in different matrices with the Zeeman atomic absorption spectrophotometer, model 5000 and atomization from tube wall.

CHARACTERIZATION TIMES (ms)					
	Cr VI IN PURE WATER	Cr VI IN SYN- THETIC SEAWATER SOLUTION	Cr VI IN NaCl AQUEOUS SOLUTION	Cr VI IN MgCl ₂ AQUEOUS SOLUTION	Cr VI IN CaCl ₂ AQUEOUS SOLUTION
$\tau_{app.}$	533	467	333	667	483
τ_1	500	350	484	366	217
τ_2	754	585	774	663	710
τ_1/τ_2	0.66	0.60	0.63	0.55	0.31

3.3- X-RAY DIFFRACTION ANALYSIS

Several investigators have reported valuable additional information on atom formation using physico-chemical techniques including AES (Auger Electron Spectroscopy), SEM (Scanning Electron Microscopy), XRD (X-Ray Diffraction) (63) and Ion Microprobe (64), which have identified condensed-phase precursors to $M_{(g)}$.

X-ray diffraction analysis is used in order to confirm detailed mechanisms of atomization. Thermodynamic parameters are often insufficient to confirm proposed mechanisms. In this study, the X-ray diffraction spectra of the sample residues left as a result of charring the samples at different charring temperatures were compared with the standard X-ray diffraction data (55) to identify the species in the condensed phase.

Table 10 shows the standard X-ray diffraction data used for identifying the chromium species formed when aqueous solutions of Cr (VI) (taken as $K_2Cr_2O_7$) were atomized from the surface of pyrolytic graphite platforms in the graphite furnace at different charring temperatures as a function of heating time. Figure 6 shows the species formed by chromium VI (taken as $K_2Cr_2O_7$) in pure water and in synthetic seawater, as a function of the charring temperature.

In Fig. 6, in the case of chromium VI in pure water, the $K_2Cr_2O_7$ was converted into $Cr_2O_3(s)$ during the charring step below $1400^\circ C$ (appearance temperature for chromium) just prior to the atomization step. The sample of chromium VI in synthetic seawater was in reality a solution of $K_2Cr_2O_7$ in diluted synthetic seawater. At tem-

peratures below 1300°C , the Cr-species formed was identified as $\text{NaCrO}_2(\text{s})$. At temperatures higher than 1300°C , $\text{NaCrO}_2(\text{s})$ was converted into $\text{Cr}_2\text{O}_3(\text{s})$, which was the final precursor of $\text{CrO}(\text{g})$.

In order to prove that the charring time did not cause significant change in the identity of the species, two pre-atomization times (45 sec. and 90 sec.) were selected while keeping the charring temperature constant at 1200°C . For chromium VI in synthetic seawater, the species found were the same $\text{NaCrO}_2(\text{s})$. However, since the X-ray diffraction analysis was done after the reaction product inside the graphite furnace was cooled down to room temperature, it could not be concluded with any certainty that the reaction product actually formed at high temperatures inside the graphite furnace was the same as present in the sample at the room temperature and analyzed with the X-ray diffractometer.

Table 10 . Standard X-ray diffraction data used for identifying chromium species formed at different charring temperatures on graphite platforms in the graphite furnace.

SPECIES IDENTIFIED	D-SPACINGS IDENTIFIED AND RELATIVE INTENSITIES (%) GIVEN IN PARENTHESIS	
$\text{NaCrO}_2(\text{s})$	5.320 (70)	2.451 (40)
	2.662 (20)	2.164 (100)
	2.542 (20)	2.005 (2)
$\text{Cr}_2\text{O}_3(\text{s})$	3.633 (75)	2.666 (100)
	2.480 (95)	2.264 (12)
	2.176 (40)	2.048 (10)
	1.816 (40)	1.672 (90)
	1.465 (25)	1.431 (40)

3.4. DUAL-CAVITY PLATFORM

Investigation into whether the reaction causing the matrix interference occurred in the condensed phase (18,68) or in the vapour (69) was done using a dual-cavity, graphite platform (48) in graphite furnace atomic absorption spectrometry. The function of a dual-cavity platform is to avoid mixing of the analyte and the potential interferents in the condensed phase.

The Perkin-Elmer atomic absorption spectrophotometer, model 5000, equipped with a Zeeman background correction system, and an HGA-500 graphite furnace were used for this experiment.

The effect of the synthetic seawater matrix on the chromium signal was studied using a dual-cavity graphite platform in order to obtain more information about the mechanisms of interference and to understand the cause and the nature of the observed enhancement effect on the analyte signal. A graphite platform having two cavities for holding the sample and the potential interferent was used. Separate experiments were done in which the analyte and the interferent were in turn atomized from the same cavity, and the separate cavities, and also, the analyte was atomized alone in one cavity.

Figure 12 and Table 11 show that 2.5×10^{-12} kg of chromium VI in pure water gave peak-height and peak-area absorbances of 0.716 and 1.215, respectively, at the optimum charring and atomization temperatures. For 2.5×10^{-12} kg of chromium VI and 1.5×10^{-7} kg of the salt matrix of synthetic seawater placed in separate cavities, peak-height and peak-area absorbances were 0.726 and 1.296, respec-

vely, at the optimum charring and atomization temperatures. Peak-height and peak-area absorbances for chromium VI in synthetic seawater placed in the same cavity were 1.07 and 1.662, respectively, at the same optimum charring and atomization temperatures.

Figure 12 shows that if chromium VI and synthetic seawater are pipetted into and atomized from separate cavities, the signals are identical to that of chromium VI in pure water, suggesting that the reactions in the vapour phase between the chromium VI and the matrix does not cause the observed interference. It is therefore reasonable to conclude that reactions between chromium VI and the synthetic seawater matrix occurs in the condensed phase, resulting in the observed interference.

Table 11. Determination of peak-height and peak-area absorbances of 2.5×10^{-12} kg of chromium VI in pure water and in synthetic seawater deposited in different cavities in a dual-cavity graphite platform.

	PEAK-HEIGHT,	PEAK-AREA,	CHARRING	ATOMIZATION
	A	A.s	TEMPERATURE	TEMPERATURE
			(°C)	(°C)
CHROMIUM VI IN PURE WATER	0.716	1.215	900	2600
CHROMIUM VI IN SYNTHETIC SEA- WATER DEPOSITED IN TWO SEPARATE CAVITIES	0.726	1.296	1100	2600
CHROMIUM VI IN SYNTHETIC SEA- WATER DEPOSITED IN THE SAME CAVITY	1.07	1.662	1100	2600

Figure 12. Absorbance signals of 2.5×10^{-12} kg of chromium VI obtained using the Zeeman atomic absorption spectrophotometer, model 5000, and a dual-cavity platform.

3.5. MECHANISMS OF ATOMIZATION OF CHROMIUM FROM THE GRAPHITE TUBE WALL.

Based on the model proposed by B. Smets (42), in which the logarithm of the calculated k_1 was plotted as a function of the reciprocal of the absolute temperature, the activation energy (E_a) of the rate-determining step in the sequence of reactions leading to the atomization of chromium VI in pure water and in synthetic seawater was determined.

It was assumed that a gas phase-condensed phase equilibrium was established in the furnace and the production of atoms was characterized by a first-order rate constant. The magnitude of the activation energy (E_a) is an excellent approximation to the bond dissociation energies of gaseous species because the activation energy (E_a) for the unimolecular decomposition of molecules in which the fission of one bond results in the production of two atoms is equal to the dissociation energy of the broken bond (70).

The activation energy (E_a) of atomization may be correlated with one of the following values:

- The heat of atomization of the metal compound
- The heat of vaporization of the metal (liquid)
- The heat of sublimation of the metal (solid)
- The dissociation energy of the metal halide
- The dissociation energy of the metal-carbon bond
- The dissociation energy of the metal oxide
- Carbon reduction of the metal oxide
- The dissociation energy of the metal dimer

Figures 13a, 14b, 15a and 16b (a = day 1, b = day 2) show the absorbance signal of 2.5×10^{-11} kg of chromium VI in pure water and in synthetic seawater and the temperature profiles recorded with a digital oscilloscope. Figures 17a, 18b, 19a, and 20b (a = day 1, b = day 2) show the measured activation energies for chromium VI in pure water and in synthetic seawater. The average of the activation energies values measured on two different days for chromium VI in pure water was $395 \pm 2 \text{ kJ mol}^{-1}$. From the slope of the plot of natural logarithm of absorbance versus the reciprocal of the absolute temperature, R.E. Sturgeon et al. (71) have found an activation energy of 410 kJ mol^{-1} , which is slightly higher than the heat of vaporization of the element, $398 \pm 4 \text{ kJ mol}^{-1}$. The latter value is in good agreement with the measured value ($395 \pm 2 \text{ kJ mol}^{-1}$).

The average of the activation energy values measured on two different days for chromium VI in synthetic seawater was $432 \pm 20 \text{ kJ mol}^{-1}$, which was about 10 % higher than that of chromium VI in pure water. The above difference in the activation energies might be due to a difference in the atomization mechanism of chromium VI in the two matrices.

Table 12 shows a comparison of the literature values of ΔH^θ for different reactions with the experimental activation energies. Since the standard deviations of the measurements for the activation energies values were ± 2 for pure water and ± 20 for synthetic seawater, the 95% confidence levels for the activation energies values were $395 \pm 4 \text{ kJ mol}^{-1}$ and $432 \pm 40 \text{ kJ mol}^{-1}$, respectively. The

above confidence level allows unquestionable correlation for the activation energies value of $395 \pm 4 \text{ kJ mol}^{-1}$ for Cr (VI) in pure water with a single reaction - reaction No. 1 of Table 12. However, for the activation energy value of $432 \pm 40 \text{ kJ mol}^{-1}$ for Cr (VI) in synthetic seawater, both reactions No. 1 and No. 5 are possible. Also, Table 13 shows that reactions No. 1 and No. 5 are thermodynamically favourable at the appearance temperatures of chromium VI, which are 1670 K for Cr VI in pure water and 1990 K for Cr (VI) in synthetic seawater.

Tables 13 and 14 show that the reduction of $\text{Cr}_2\text{O}_3(\text{s})$ by carbon is highly favourable ($\Delta G < 0$) at the appearance temperature of Cr VI in pure water ($\sim 1700 \text{ K}$), with a $\Delta G = -78.12 \text{ kJ mol}^{-1}$. Moreover, the results of X-ray diffraction analysis support the presence of $\text{Cr}_2\text{O}_3(\text{s})$ in the condensed phase in the pre-atomization step. Hence, the mechanism for the atomization of chromium from pure water is proposed as follows:

Table 12. ΔH^θ of chromium VI for different reactions compared with the experimental activation energies.

ΔH^θ (kJ mol ⁻¹)							ACTIVATION ENERGY	
1	2	3	4	5	6	7	(kJ mol ⁻¹)	
							IN PURE WATER	IN SYNTHETIC SEA-WATER
398	255	366*	1275	427*	1605	324	395	432
							$\pm 2^{**}$	$\pm 20^{**}$

* Bond Dissociation Energy (D_{298}^θ) (72)

** Standard Deviation

Table 13. Change in free energy (ΔG) for different reactions at
1700 K.*

REACTIONS	ΔG_r (kJ mol ⁻¹)
$\text{Cr}_{(s)} \text{-----} \rightarrow \text{Cr}_{(g)}$	-56
$\text{Cr}_{(l)} \text{-----} \rightarrow \text{Cr}_{(g)}$	+146
$\text{Cr}_3\text{C}_{2(s)} \text{-----} \rightarrow 3 \text{Cr}_{(g)} + 2 \text{C}_{(s)}$	-108**
$\text{CrO}_{(g)} \text{-----} \rightarrow \text{Cr}_{(g)} + 1/2 \text{O}_{2(g)}$	-444**
$\text{Cr}_2\text{O}_3(s) + 3 \text{C}_{(s)} \text{-----} \rightarrow 2 \text{Cr}_{(s)} + 3 \text{CO}_{(g)}$	-78

* Ref: (41,75,76,77)

** At 2000 K

$$P_{\text{CO}_{(g)}} = 4 \times 10^{-4} \text{ atm.}$$

$$P_{\text{O}_{2(g)}} = 1.8 \times 10^{-22} \text{ atm.}$$

ΔG_r = free energy change for the reactions

Table 14. Change in free energy (ΔG) for chromium atom formation
from chromium VI in pure water by carbon reduction.

TEMPERATURE (K)	1	2	3	4	5	6
	kJ mol ⁻¹					
1400	-62.21	-419.69	-1368.21	-24.09	+56.98	-
1500	-69.23	-444.39	-1395.45	-27.39	+ 5.99	-
1600	-76.52	-469.92	-1423.52	-30.84	-44.96	-
1700	-84.07	-494.48	-1452.48	-34.44	-95.78	-72.18
1800	-91.88	-519.83	-1482.18	-38.18	-146.53	-

• Ref: (41, 75, 76, 77)

$$1 = \Delta G_f^\theta(\text{Cr}(\text{s}))$$

$$2 = \Delta G_f^\theta(\text{CO}(\text{g}))$$

$$3 = \Delta G_f^\theta(\text{Cr}_2\text{O}_3(\text{s}))$$

$$4 = \Delta G_f^\theta(\text{C}(\text{s}))$$

$$5 = \Delta G_r^\theta$$

$$6 = \Delta G_r$$

At 1700 K, $P_{\text{CO}(\text{g})} = 3.4 \times 10^{-4}$ atm.

ΔG_f^θ = standard free energy change
for the formation

ΔG_r^θ = standard free energy change
for the reaction

In Tables 13 and 14, the relationship between ΔG and ΔG^θ for the reaction:

is given by equation 29:

$$\Delta G = \Delta G^\theta + RT \ln \frac{\prod_{i=1}^m a_i^{t_i}}{\prod_{i=1}^k a_i^{r_i}} \quad 29$$

where a is the activity of the substance.

Equation 29 has been used to determine the spontaneity of reactions at the appearance temperature (which is defined as the minimum temperature at which the atomic absorption signal just becomes detectable above the baseline (44)). Estimates of partial pressure of gases (CO , CO_2 , O_2) at equilibrium in the graphite furnace were taken from C.L. Chakrabarti et al. (41) at the appearance temperature and for a graphite furnace of the same volume (8×10^{-4} L) as the graphite furnace used in this work.

It should be noted that the melting point of the chromium oxide (Cr_2O_3 (s)) is 2266°C (72). Thus, the chemical form expected is Cr_2O_3 (s) because the appearance temperature is 1400°C for chromium VI in pure water and 1720°C for chromium VI in synthetic seawater.

For chromium VI in synthetic seawater, the results of X-ray diffraction analysis confirm the presence of $\text{Cr}_2\text{O}_3(s)$ and $\text{NaCrO}_2(s)$ in the condensed phase at pre-atomization temperatures of 1400 - 1500 K and 1100 - 1300 K, respectively, as the precursors of $\text{Cr}(g)$ atoms. The probability that $\text{NaCrO}_2(s)$ is thermally more stable may explain the observed shift in the appearance temperature from 1670 K to 1990 K in the thermal decomposition-atomization curves for chromium VI in synthetic seawater relative to those for chromium VI in pure water.

Based on the value of the experimental activation energy (E_a) and the results of X-ray diffraction analysis, two possible mechanisms for atomization of chromium VI in synthetic seawater in graphite furnace atomic absorption spectrometry are proposed as follows:

MECHANISM I

MECHANISM II

Since the amounts of chromium taken for thermal decomposition-atomization curves are lower by about 4 orders of magnitude than those used for the X-ray diffraction (XRD) analysis, it cannot be said with complete certainty that the proposed mechanisms apply also to the usual analytical amounts of chromium (μg to ng). However, the observed correlation of the experimental activation energies with the heats of various possible chemical reactions, and the corroborative evidence of the XRD analysis lead to the conclusion that the atomization mechanisms postulated above are reasonable.

Figure 13a. Absorbance signal of 2.5×10^{-11} kg of chromium VI in synthetic seawater (1) and the temperature profile (2) recorded with a digital oscilloscope (day 1).

Figure 14b. Absorbance signal of 2.5×10^{-11} kg of chromium VI in synthetic seawater (1) and the temperature profile (2) recorded with a digital oscilloscope (day 2).

Figure 15a. Absorbance signal of 2.5×10^{-11} kg of chromium VI in pure water (1) and the temperature profile (2) recorded with a digital oscilloscope (day 1).

Figure 16b. Absorbance signal of 2.5×10^{-11} kg of chromium VI in pure water (1) and the temperature profile (2) recorded with a digital oscilloscope (day 2).

Figure 17a. The Arrhenius plot for chromium VI in synthetic seawater (day 1).

Figure 18b. The Arrhenius plot for chromium VI in synthetic seawater (day 2).

2 of/de 2

Figure 20b. The Arrhenius plot for chromium VI in pure water
(day 2).

3.6. MECHANISMS OF ATOMIZATION OF CHROMIUM AT CONSTANT TEMPERATURE IN THE GRAPHITE PROBE FURNACE.

The graphite probe furnace atomic absorption spectrometric technique has been used to establish conditions for isothermal (temporal) atomization using the commercial, semi-enclosed pulse-heated, graphite tube furnace mentioned earlier. The mechanism of heating of the graphite probe furnace is primarily by radiation heat transfer from the heated tube wall. The graphite probe is inserted into the graphite furnace only after it has attained a final, steady-state temperature. The probe is inserted very rapidly (takes 5 ms) into the furnace, and for the sake of simplicity, no heat transfer is considered for the duration of the insertion. Theoretical analysis has shown that heat transfer by convection and conduction through the argon gas in the furnace is insignificant compared to heat transfer by radiation (51,79). Moreover, the steady-state tube wall temperature at the furnace centre is responsible for the heating of the probe by radiation because the probe is inserted into the central part of the furnace where the tube wall has no appreciable temperature gradient in the axial direction and the furnace heating control keeps the wall temperature at the furnace centre invariant with time (51,79).

Figures 21 and 22 show respectively, the absorbance profiles of chromium VI, taken as potassium dichromate in an aqueous solution, and in synthetic seawater, using different temperatures and sample atomization from the graphite probe surface. The absorbance profiles were recorded with the Perkin-Elmer Professional Computer, model 7500.

A Perkin-Elmer computer program was used in order to obtain the absorbance signal for chromium VI in pure water and in synthetic seawater, both vs time, and graphs were drawn using a logarithmic scale for the ordinate (Figs. 23-26 for chromium VI in pure water and Figs. 27-30 for chromium VI in synthetic seawater). The rate constant for chromium atom loss (k_2) (curve C in Figs. 23-26 and curve B in Figs. 27-30) was obtained from the slope of the straight line drawn through the experimental data points located at the tail of the absorbance signal. The rate constant for chromium atom formation, (k_1) was obtained from the slope of the straight line drawn by using the difference between the extrapolated absorbance and the experimental absorbance at any time (t). The slopes were calculated by least-squares linear regression analysis. The precision of any rate constant value was no better than 10% relative standard deviation (RSD) as the absorbance values used in k_1 and k_2 calculations had that order of relative precision.

In some cases (e.g., Figs. 23-26), the straight line corresponding to earlier times and having the lower slope (curve A), gives the value of the rate constant (k_1), and the straight line (curve B) corresponding to later times and having a steeper slope yields the sum of the rate constants i.e., ($k_1 + k_3$) for the combined mode of decrease of the pre-atomization species A, where C' is the product of the other loss process of species A as shown below:

where k_3 is the first-order rate constant for the loss of Cr_2 dimeric species through the sample injection hole.

Figures 31 and 32 show the Arrhenius plots, obtained by plotting the natural logarithm of the rate constant for chromium atom formation (s^{-1}) vs the reciprocal of the absolute temperature ($1/T(\text{K})$). The slope of these plots gives the activation energy (E_a). Three different temperatures, as described below, were measured and used in drawing the Arrhenius plots in order to have a better approximation of the unknown temperature involved in the actual atomization process. The tube wall temperature was measured directly by using an optical pyrometer, the probe surface temperature was determined by using a computer simulation program (78), the effective, steady-state gas temperature of the vapour phase in the graphite probe furnace was determined by the two-line atomic absorption method using the Sn 286.3/284.0 nm line pair (Fig. 33) (51,79). The last method involved measuring the atom population ratio in terms of the absorbance values given by atoms of the same element for two different lines. The atom population ratio was then related to the effective vapour temperature using the reduced equation as shown below (51,79):

(51,79):

$$T_{\text{eff}} = \frac{2143}{\log (4.9 A_1 / A_2)}$$

30

where

A_1 = absorbance of Sn at 286.3 nm

A_2 = absorbance of Sn at 284.0 nm

Table 15 shows the activation energies for chromium VI in pure water and in synthetic seawater obtained by using the above-mentioned different temperatures. For chromium VI in pure water, the activation energy was obtained by using the tube wall temperature, the gas phase temperature and the probe temperature was $353 \pm 2 \text{ kJ mol}^{-1}$, $360 \pm 0 \text{ kJ mol}^{-1}$ and $338 \pm \text{kJ mol}^{-1}$, respectively. These values were the averages of two determinations made on two different days. The arithmetic mean of the above three values was $350 \pm 13 \text{ kJ mol}^{-1}$. The Arrhenius plot for chromium VI in pure water (Fig. 31) shows that the straight line obtained by using the probe surface temperature has the lowest slope (triangles), and that obtained by using the tube wall temperature has the highest slope (circles).

For chromium VI in synthetic seawater, the activation energy was obtained by using the tube wall temperature, the gas phase temperature and the probe surface temperature was $1230 \pm \text{kJ mol}^{-1}$, $1110 \pm 98 \text{ kJ mol}^{-1}$ and $980 \pm \text{kJ mol}^{-1}$, respectively. The arithmetic mean of these three values was $1107 \pm 99 \text{ kJ mol}^{-1}$.

The Arrhenius plot (Fig. 32) for chromium VI in synthetic

seawater shows that the slope obtained using the tube wall temperature (circles) has a higher value than the slopes of the two others (the gas phase temperature (squares) and the probe surface temperature (triangles) , and that the value obtained using the probe surface temperature is the lowest. Moreover, Fig. 32 shows the same order for the values of temperature: the gas phase temperature, the tube wall temperature and the probe surface temperature. The probe was heated by radiation heat transfer only; and acted as a heat sink. Hence, its initial temperature was less than that of the tube wall, and the temperature approached the tube wall temperature only at longer times. The vapour temperature inside the furnace was high and constant at the time of insertion of the cold probe; the latter lowered the temperature of the vapour phase immediately surrounding it.

The arithmetic mean values of activation energies for chromium VI are compared with the ΔH^θ values for different possible reactions that can occur in the graphite furnace, as shown in Table 12. For chromium VI in pure water, the arithmetic mean of the above three values of the activation energy (350 kJ mol^{-1}) correlates well with the dissociation energy of Cr_2 dimeric species:

The mechanism of atomization for chromium VI in pure water in the graphite probe furnace involves dissociation of Cr_2 dimeric species and can be postulated as follows:

For chromium VI in synthetic seawater, the mechanism of atomization in the graphite probe furnace was evidently different. The arithmetic mean value of the activation energy was $1107 \pm 99 \text{ kJ mol}^{-1}$ compared with $432 \pm 20 \text{ kJ mol}^{-1}$ for the tube wall atomization with the Perkin-Elmer Heated Graphite Atomizer, model 2100. The activation energy obtained using the graphite probe ($1107 \pm 99 \text{ kJ mol}^{-1}$) correlates well with the ΔH^θ for the following reaction (shown in Table 12):

The reaction is atomization of chromium carbide ($\text{Cr}_3\text{C}_2(\text{s})$) from the surface of the graphite probe in the graphite furnace. The mechanism of atomization for chromium VI in synthetic seawater in the graphite probe furnace can be postulated as follows:

The above mechanism is consistent with the fact that the free energy change (ΔG) (Table 13) shows that the dissociation of chromium carbide ($\text{Cr}_3\text{C}_2(\text{s})$) is thermodynamically favourable at the appearance temperature (2000 K) of chromium VI.

Table 15. Activation energies for atomization of chromium VI
in pure water and in synthetic seawater obtained
using different temperatures.

THE TEMPERATURE USED IN DRAWING THE ARRHENIUS PLOT	E_a , kJ mol ⁻¹	E_a , kJ mol ⁻¹
	Cr VI IN SYNTHETIC SEAWATER	Cr VI IN PURE WATER
TUBE WALL TEMPERATURE	1230 $\pm$ 88	353 $\pm$ 2
GAS PHASE TEMPERATURE (1)	1110 $\pm$ 98	360 $\pm$ 0
PROBE SURFACE TEMPERATURE (2)	980 $\pm$ 255	338 $\pm$ 13

1- Ref: 52

2- Ref: 76

Figure 21. Absorbance profiles of chromium VI in pure water at different temperatures (° C) using the graphite probe furnace with the atomic absorption spectrophotometer, model 5000.

Figure 22. Absorbance profiles of chromium VI in synthetic seawater at different temperatures ($^{\circ}\text{C}$) using the graphite probe furnace with the atomic absorption spectrophotometer, model 5000.

Figure 23. Plot of log absorbance vs time for chromium VI in pure water at 2700 °C. Curve A straight line giving slope = $-k_1 / 2.303$, curve B : straight line giving slope = $-(k_1 + k_3) / 2.303$, curve C : straight line giving slope = $-k_2 / 2.303$.

Figure 24. Plot of log absorbance vs time for chromium VI in pure water at 2600°C. Curve A : straight line giving slope = $-k_1 / 2.303$, curve B : straight line giving slope = $-(k_1 + k_3) / 2.303$, curve C : straight line giving slope = $-k_2 / 2.303$.

Figure 25. Plot of log absorbance vs time for chromium VI in pure water at 2500 °C. Curve A : straight line giving slope = $-k_1 / 2.303$, curve B : straight line giving slope = $-(k_1 + k_3) / 2.303$, curve C : straight line giving slope = $-k_2 / 2.303$.

Figure 26. Plot of log absorbance vs time for chromium VI in pure water at 2400 °C. Curve A: straight line giving slope = $-k_1 / 2.303$, curve B: straight line giving slope = $-(k_1 + k_3) / 2.303$, curve C straight line giving slope = $-k_2 / 2.303$.

Figure 27. Plot of log absorbance vs. time for chromium VI in synthetic seawater at 2600 °C. Curve A straight line giving slope = $-k_1 / 2.303$, curve B straight line giving slope = $-k_2 / 2.303$.

Figure 28. Plot of log absorbance vs time for chromium VI in synthetic seawater at 2500 °C. Curve A : straight line giving slope = $-k_1 / 2.303$, curve B : straight line giving slope = $-k_2 / 2.303$.

Figure 29. Plot of log absorbance vs time for chromium VI in synthetic seawater at 2400 °C. Curve A : straight line giving slope = $-k_1 / 2.303$, curve B : straight line giving slope = $-k_2 / 2.303$.

Figure 30. Plot of log absorbance vs time for chromium VI in synthetic seawater at 2350 °C. Curve A straight line giving slope = $-k_1 / 2.303$, curve B straight line giving slope = $-k_2 / 2.303$.

Figure 31. The Arrhenius plot for chromium VI in pure water using the three different temperatures. $\square$ effective (steady-state) gas phase temperature, $\circ$ tube wall temperature, $\triangle$ probe temperature.

Figure 32. The Arrhenius plot for chromium VI in synthetic seawater using the three different temperatures.
 □ effective (steady-state) gas phase temperature,
 ○ tube wall temperature, △ probe temperature.

Figure 33. Effective (steady-state) gas temperature in the graphite probe furnace as a function of the final tube wall (atomization) temperature, determined by the two-line atomic absorption method using Sn 286.3/284.0 nm line pair.

3.7. ATOMIZATION EFFICIENCY

Table 16 shows the atomization efficiency values and first-order rate constants for atom formation and atom loss for chromium VI in pure water in the Perkin-Elmer Heated Graphite Atomizer, model 500. The atomization temperatures chosen were 2870, 2770, 2670 and 2570 K. The appearance temperature for chromium VI in pure water was 1670 K. The heating rate was calculated from Fig. 34 using the straight-line part of the temperature-time curve (40 ms).

$$\text{HEATING RATE} = \frac{T_1 - T_{\text{app}}}{(t_1 - t_{\text{app}})} \quad 31$$

where

T_{app} = the appearance temperature (K)

t_{app} = the appearance time (ms)

T_1 = the temperature (K) at time t_1 (ms)

Figure 35 (the enlargement of the temperature profile at 2600 °C) shows the appearance temperature for chromium VI in pure water (A), and for chromium VI in synthetic seawater (B).

The heating rate is one of the important factors that determine the rate of atom formation at the leading edge of the atomic absorption pulse (45,77). The maximum heating rate that

was obtainable from the power supply and used was about 1.4 K ms^{-1} .

In order to get good absorbance signals, a narrow range of temperature was used. The values of k_1 and k_2 (first-order rate constants for atom formation and atom loss, respectively) and β_1 and β_2 (atomization efficiencies) were calculated from the absorption pulses presented in the previous section. As can be seen from equation 32 (below), in order to get a high atomization efficiency, β_1 , $(k_2 t_{\max})$ should be made as small as possible. For chromium VI in pure water, low values of k_2 (0.7 s^{-1}) were obtained at moderately high atomization temperatures (2670 and 2570 K), whereas $t_{\max}$ is high at these temperatures. However, the β_1 and β_2 values are consistent. The average values for β_1 and β_2 are 0.48 and 0.45, respectively. The maximum atomization efficiency β_1 (0.57) was obtained using a high (but constant) heating rate and a moderately high atomization temperature.

$$\beta_1 = \exp(-k_2 t_{\max}) \quad 32$$

The measured β_1 values were compared with the calculated β_1 values - the latter values were calculated by using equation 32. The values of $t_{\max}$ were calculated by using equation 33:

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad 33$$

The calculated $t_{\max}$ values obtained using equation 33 were approximatively the same as the measured $t_{\max}$ values and yielded the same atomization efficiency values. The measured $t_{\max}$ values were obtained using a Perkin-Elmer computer program which provided accurate measurements of $t_{\max}$, and hence, gave accurate values for β_1 . Hence, the measured β_1 values were as reliable as the calculated β_1 values.

Table 17 shows the atomization efficiency values and first-order rate constants for atom formation and atom loss for chromium VI in synthetic seawater. The appearance temperature was 1990 K. The atomization temperatures were the same as in Table 16 except for the last temperature (2620 K). The heating rate was kept constant at 1.4 K ms^{-1} .

Table 16. Atomization efficiency values and first-order rate constants for atom formation and atom loss for chromium VI in pure water using the Perkin-Elmer HGA-500 and the graphite probe furnace.

ELEMENT	ATOMIZATION TEMPERATURE (K)	APPEARANCE TEMPERATURE (K)	HEATING RATE (K/ms)	CALCULATED		MEASURED		k_1 (s^{-1})	k_2 (s^{-1})	$k/k_{1/2}$	MEASURED t_{max}
				t_{max}	β_1	β_1	β_2				
CHROMIUM VI IN PURE WATER	2870			0.420	0.47	0.36	0.36	3.2	1.8	1.8	0.567
	2770			0.653	0.46	0.48	0.43	2.1	1.2	1.8	0.617
	2670	1670	1.4	0.925	0.52	0.57	0.49	1.6	0.7	2.3	0.800
	2570			0.925	0.52	0.51	0.53	1.6	0.7	2.3	0.950

Table 17. Atomization efficiency values and first-order rate constants for atom formation and atom loss for chromium VI in synthetic seawater using the Perkin-Elmer HGA-500 and the graphite probe furnace.

ELEMENT	ATOMIZATION TEMPERATURE (K)	APPEARANCE TEMPERATURE (K)	HEATING RATES (K/ms)	CALCULATED		MEASURED		k		k/k	MEASURED t_{max} (s)		
				t_{max}	β_1	β	β	1	2			1	2
CHROMIUM VI IN SYNTHETIC SEAWATER	2870			0.180	0.72	0.48	0.71	12.7	1.8	7.1	0.411		
	2770	1990	1.4	0.269	0.69	0.42	0.40	7.8	1.4	5.6	0.619		
	2670			0.334	0.74	0.51	0.39	7.1	0.9	7.9	0.759		
	2620			0.786	0.58	0.48	0.48	2.1	0.7	3.0	1.050

Figure 34. Absorbance profile of chromium VI in pure water (1) and the temperature profile (2) of the graphite tube wall recorded with a digital oscilloscope using the graphite probe furnace with the atomic absorption spectrophotometer, model 5000. The steady-state (plateau) temperature of the graphite tube wall was 2600°C .

Figure 35. Enlargement of the temperature profile shown in Fig.

34. A and B are the appearance temperatures for chromium VI in pure water and in synthetic seawater, respectively.

CONCLUSIONS

In graphite furnace atomic absorption spectrometry, the sensitivity of chromium determination is independent of the oxidation state of chromium. Thermal decomposition-atomization curves for chromium VI in pure water and in synthetic seawater show that the appearance temperature of chromium VI in synthetic seawater is 1990 K compared to 1670 K for chromium VI in pure water. Peak-height absorbance for chromium VI in synthetic seawater shows an enhancement of about 45% compared to the chromium VI in pure water. Peak-area absorbance for chromium VI in synthetic seawater and in pure water is about the same.

The effects of different chloride matrices on the chromium VI peak-height signal show that the NaCl matrix reduces the peak-height signal of chromium VI in pure water, the $MgCl_2$ and the $CaCl_2$ matrix, and the synthetic seawater matrix enhance the chromium peak-height signal. The depressive interference by the NaCl matrix on the chromium peak-height signal can be explained as follows. In the sodium chloride matrix, chromium forms chromic chloride which is co-volatilized with the bulk of the sodium chloride matrix at 800 - 900 °C and is partially expelled from the graphite tube along with the rapidly expanding sodium chloride vapour, resulting in a partial loss of chromium through the sample injection hole (58). The enhancement effect of the $CaCl_2$ and the $MgCl_2$ matrix may be due to the fact that although the same chromium chloride is formed in the calcium or the magnesium chloride matrix, these matrices are vaporized at a much higher temperature than the NaCl matrix, this prevents the partial loss of

of chromium (as chromium chloride), and also allows a more rapid (kinetic factor), or a more complete dissociation of $\text{CrCl}_3(\text{g})$ (thermodynamic factor).

Characterization times of the absorption pulses for chromium VI show mainly a lower atomization time (τ_1) (350 ms) for chromium VI in synthetic seawater than chromium VI in pure water (500 ms).

X-ray diffraction analysis confirms the presence of $\text{Cr}_2\text{O}_3(\text{s})$ in the pre-atomization step (condensed phase) for chromium VI in pure water at a temperature below 1500°C . For chromium VI in synthetic seawater, the species $\text{NaCrO}_2(\text{s})$ has been identified at a temperature below 1300°C . The $\text{NaCrO}_2(\text{s})$ is converted into $\text{Cr}_2\text{O}_3(\text{s})$ at higher temperatures (between 1300°C and 1600°C).

The results of the study using a dual-cavity, graphite platform suggest that the chloride matrix interference occurs in the condensed phase.

In the tube wall atomization technique, the activation energy for chromium VI in synthetic seawater was found to be higher (432 kJ mol^{-1}) compared to the activation energy of chromium VI in pure water (395 kJ mol^{-1}). But, two different mechanisms for the formation of gaseous chromium atoms was proposed in the above two cases. The atomization of chromium VI in pure water from a graphite tube wall surface involves the heat of vaporization of $\text{Cr}(\text{s})$ - the reaction is thermodynamically favourable at the appearance temperature of 1700 K . The atomization of chromium VI in synthetic seawater involves the dissociation energy of $\text{CrO}(\text{g})$ - the dissociation is

thermodynamically favourable at the appearance temperature of 2000 K.

The activation energy for chromium VI in pure water (350 kJ mol^{-1}) with the graphite probe furnace was lower than the value obtained with tube wall atomization (395 kJ mol^{-1}). The difference in the activation energies was significant, and a different atomization mechanism was proposed. For chromium VI in synthetic seawater, the chloride matrix alters the atomization mechanism of chromium VI in the graphite probe furnace, giving an activation energy of 1107 kJ mol^{-1} , which corresponds to the chromium-carbide bond dissociation energy - the vapour phase dissociation being thermodynamically favourable at the appearance temperature of 2000 K.

The results from the atomization efficiency for chromium VI in pure water with the graphite probe furnace have shown a maximum atomization efficiency (β_1) of 0.57 at 2670 K, whereas in synthetic seawater the maximum atomization efficiency (0.51) was obtained at the same temperature of 2670 K.

REFERENCES

1. W. Mertz, E. W. Toepfer, E. E. Roginski and M. M. Polansky.
Federation of American Societies for Experimental Biology. Federation Proceedings, 33, 2275 (1974).
2. W. R. Wolf. Federation of American Societies for Experimental Biology. Federation Proceedings, 34, 972 (1975).
3. W. H. Allaway. In International Conference on Heavy Metals in the Environment, Toronto, Ontario, Canada, Vol. 1, 57 (1975).
4. A. K. Mathur, Satya V. Chandra and S. K. Tandon. Toxicology, 8, 53 (1977).
5. R. E. Cranston. Chromium in Cascadia Basin, Northeast Pacific Ocean, Marine Chem., 13, 109 (1983).
6. H. Elderfield. Chromium speciation in seawater, Earth Planet. Sci. Lett., 9, 10 (1970).
7. P. G. Brewer. Minor elements in seawater. In Chemical Oceanography, Vol. 1, J. P. Riley and G. Skirrow (Editors), 2nd edn, Academic Press, London, 415 (1975).
8. S. R. Koirtyohann and E. E. Pickett. Anal. Chem. 38, 585 (1966).
9. J. Smeyers-Verbeke, Y. Michotte, P. van den Winkel and D. L. Massart. Anal. Chem. 48, 125 (1976).
10. R. B. Cruz and J. C. van Loon. Anal. Chim. Acta, 72, 231 (1974).

11. D. J. Churella and T. R. Copeland. *Anal. Chem.* **50**, 309 (1978)
12. R. C. Hutton, J. M. Ottaway and T. Platt. *Federation of Analytical Chemistry and Spectroscopy Societies, Paper 307* (1976).
13. C. L. Chakrabarti, C. C. Wan, H. A. Hamed and P. C. Bertels. *Anal. Chem.* **53**, 444 (1981).
14. W. Slavin, G. R. Carnrick and D. C. Manning. *Anal. Chem.* **56**, 163 (1984).
15. T. Nakahara and C. L. Chakrabarti. *Anal. Chim. Acta*, **104**, 99 (1979).
16. J. P. Erspamer and T. M. Niemczyk. *Anal. Chem.* **54**, 538 (1982).
17. L. R. Hageman, J. A. Nichols, P. Viswanadham and R. Woodriff. *Anal. Chem.* **51**, 1406 (1979).
18. J. A. Krasowski and T. R. Copeland. *Anal. Chem.* **51**, 1843 (1979).
19. W. Slavin and D. C. Manning. *Anal. Chem.* **51**, 261 (1979).
20. D. A. Segar and J. G. Gonzalez. *Anal. Chim. Acta*, **58**, 7 (1972).
21. G. R. Carnrick, W. Slavin and D. C. Manning. *Anal. Chem.* **53**, 1866 (1981).

22. R. J. Stolzberg. In analytical methods in oceanography, T. R. Gibb, Jr. Ed., Adv. in Chem. series, No 147, Amer. Chem. Soc., 30 (1975).
23. L. Danielsson, B. Magnusson and S. Westerlund. Anal. Chim. Acta, 98, 47 (1978).
24. P. E. Paus. Fresenius Z. Anal. Chem., 264, 118 (1973).
25. R. A. A. Muzzarelli and R. Rochetti. Anal. Chim. Acta, 70, 283 (1974).
26. F. O. Jensen, J. Dolezal and F. J. Langmyhr. Anal. Chim. Acta, 72, 245 (1974).
27. E. A. Boyle and J. M. Edmond. Anal. Chim. Acta, 91, 189 (1977).
28. W. Frech and A. Cedergren. Anal. Chim. Acta, 88, 57 (1977).
29. E. J. Czobik and J. P. Matousek. Anal. Chem., 50, 2 (1978).
30. D. J. Churella and T. R. Copeland. Anal. Chem. 50, 309 (1978).
31. J. M. McArthur. Anal. Chim. Acta, 93, 77 (1977).
32. R. Guevremont. Anal. Chem., 52, 1574 (1980).
33. D. J. Hydes. Anal. Chem. 52, 959 (1980).
34. G. E. Batley and J. P. Matousek. Anal. Chem., 49, 2031 (1977).

35. H. S. Wabab and C. L. Chakrabarti. *Spectrochim. Acta*, **36B**, 475 (1981).
36. W. C. Campbell and J. M. Ottaway. *Talanta*, **21**, 837 (1974).
37. W. Frech, J. A. Persson and A. Cedergren. *Prog. Anal. Atom. Spectrosc.* **3**, 279 (1979).
38. G. Torsi and G. Tessari. *Anal. Chem.* **45**, 1812 (1973).
39. C. W. Fuller. *Analyst*, **99**, 739 (1974).
40. C. L. Chakrabarti, S. Wu and P. C. Bertels. *Spectrochim. Acta*, **38B**, 1041 (1983).
41. C. L. Chakrabarti, S. B. Chang and S. E. Roy. *Spectrochim. Acta*, **38B**, 447 (1983).
42. B. Smets. *Spectrochim. Acta*, **35B**, 33 (1980).
43. C. L. Chakrabarti, C. C. Wan, R. J. Teskey, S. B. Chang, H. A. Hamed and P. C. Bertels. *Spectrochim. Acta*, **36B**, 427 (1981).
44. R. E. Sturgeon and C. L. Chakrabarti. *Prog. Anal. Atom. Spectros.*, **1**, 5 (1978).
45. C. L. Chakrabarti, H. A. Hamed, C. C. Wan, W. C. Li, P. C. Bertels, D. C. Gregoire and S. Lee. *Anal. Chem.*, **52**, 167 (1980).

46. C. L. Chakrabarti, C. C. Wan, S. B. Chang, H. A. Hamed and P. C. Bertels. In recent Advances in Analytical Spectroscopy, Ed. K. Fuwa, Pergamon Press, Oxford and N.Y., P.103, (1982).
47. R. E. Sturgeon. Fresenius Z. Anal. Chem., **324**, 807 (1986).
48. B. Welz, S. Akman and G. Schlemmer. Analyst, **110**, 459 (1985).
49. C. L. Chakrabarti, S. Wu, R. Karwowski, S. B. Chang and P. C. Bertels. Atomic Spectroscopy, **5**, 69 (1984).
50. S. Wu. A Theoretical and Experimental Study of Platform Furnace and Probe Furnace in Graphite Furnace Atomic Absorption Spectrometry. Ph.D. Thesis, Carleton University, (1986).
51. S. Wu, C.L. Chakrabarti and J.T. Rogers. Prog. Anal. Spectrosc. **10**, 111 (1987).
52. C. L. Chakrabarti, S. B. Chang, S. R. Lawson and S. M. Wong. Spectrochim. Acta, **38B**, 1287 (1983).
53. J. Lyman and R. Fleming. J. Marine Res., **3**, 134 (1940).
54. S. B. Chang. Studies on the Analytical Chemistry of Chromium in Aqueous Solutions, M.Sc. Thesis, Carleton University, (1980).
55. X-Ray Powder Diffraction File, Inorganic Phases. Compiled by the Joint Committee on Powder Diffraction Standards, Published by JCPDS International Center for Diffraction Data, Philadelphia, USA (1982).

56. R. E. Sturgeon, C. L. Chakrabarti and C. H. Langford. Anal. Chem. **48**, 1792 (1976).
57. S. B. Chang and C. L. Chakrabarti. Prog. Anal. Atom. Spectrosc., **8**, 2 (1985).
58. B. V. L'vov. Spectrochim. Acta, **33B**, 153 (1978).
59. J. P. Matousek. Prog. Anal. Atom. Spectrosc. **4**, 247 (1981).
60. E. Scroll, Z. Anal. Chem. **198**, 40 (1963).
61. J. P. Matousek. Spectrochim. Acta, **39B**, 205 (1984).
62. C. W. Fuller. Proc. Anal. Div., Chem. Soc., **13**, 273 (1976).
63. B. V. L'vov. Atomic Absorption Spectrochemical Analysis, Adam Hilger Ltd. London (1970).
64. Wim M. G. T. van den Broek and Leo de Galan. Anal. Chem., **49**, 2176 (1977).
65. S. Wu, C. L. Chakrabarti, F. Marcantonio and K. L. Headrick. Spectrochim. Acta, **41B**, 651 (1986).
66. C. L. Chakrabarti, D. Ferrarotto, S. J. Cathum and C. J. Rademeyer. Canadian Journal of Chemistry, **65**, 1079 (1987).
67. B. Hircg. Spectrochim. Acta, **31B**, 153 (1976).

68. W. Frech, E. Lundberg and A. Cedergren. *Can. J. Spectrosc.*, **30**, 123 (1985).
69. W. Frech, E. Lundberg and A. Cedergren. Conference on Atomic Spectroscopy, Analytik Treffen, Neubrandburg, DDR (1982).
70. M. Szwarc. *Chem. Rev.*, **47**, 75 (1950).
71. R. E. Sturgeon. Studies on Electrothermal Atomization in Graphite Furnace Atomic Absorption Spectrometry. Ph.D. Thesis, Carleton University, (1970).
72. Handbook of Chemistry and Physics, 66th edition, R. C. Weast, Ed. Chemical Rubber Co., Cleveland, Ohio (1986).
73. C. Duval. Inorganic Thermogravimetric Analysis, Elsevier Publishing Company, N.Y., Ch. 24 (1963).
74. W. Wendl and G. Muller-Vogt. *Spectrochimica Acta*, **40B**, 527 (1985).
75. I. Barin, O. Knacke and O. Kubaschewski. Thermochemical Properties of Inorganic Substances, Springer, New York (1977).
76. JANAF Thermochemical Tables. D. R. Stull, Dow Chemical Co., Midland, Michigan (1965).
78. H. L. Shick. Thermodynamics of Certain Refractory Compounds, Academic Press, New York, 1966.
79. R. Dick. Summary of Graphite Furnace Computer Programs, Carleton University (1985).

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