SNO-STR-90- 71

LASERS IN ATOMIC SPECTROSCOPY --- MEETING REPORT

A one-day meeting with the above title was held at the University of Guildford, U.K, on Thursday 29th March 1990. The meeting was held under the auspices of the Royal Society of Chemistry and sponsored by two of its sections, the Atomic Spectroscopy Group and another called Atomic Spectrometry Updates. The RSC also publishes the Journal of Analytical Atomic Spectrometry whose title is self-explanatory. Some specimen copies of this journal were available.

The meeting programme, synopses of the talks with some added comments, list of participants and notes on some coming meetings in this field are attached. One meeting is in Canada, at Brock University, St.Catherines, Ontario, on August 1-3. It is suggested that someone involved in the radioactivity QA subproject of SNO should attend in order to find out what the current state-of-the-art is in Canada, what machines are being used and at which institutions, who is active in the field, etc. Some prior reading-up would be desirable.

I attended this meeting at Guildford for similar reasons but for two reasons in particular. In general, the whole area of analytical instrumentation is one of continuous development and the fields of atomic and mass spectrometry are certainly no exception. In view of the likely need for the QA of all materials used in the SNO detector to involve many analyses for Th,U and possibly other elements and the very lengthy timescales required for trace analyses by radioactivity counting techniques it is clearly desirable for SNO to be alert to developments in any method which has any chance of becoming sufficiently sensitive. Results produced in minutes rather than days would have many advantages. The more specific reason is that the technique known as RIMS (Resonance Ionisation Mass Spectrometry) is one of the methods thought to be possibly usable and one of the papers was on this subject.

This talk was given by Dr. Ken Ledingham of the Department of Physics and Astronomy, University of Glasgow, G12 8QQ. He outlined the basis of the technique, described the experimental equipment he had built and gave some results of measurements. I was able to have a short talk with him at the end of the meeting and told him of SNO's needs. The response was very positive and he would be interested in seeking funding to find out what the limits of detection are for thorium in various materials by this technique.

There are a large number of techniques being used and being developed, each with their own acronym, but the general impression is that the Limit of Detection (LOD) is usually determined by the SNR (Signal-to-Noise Ratio) and questions of background, reagent blanks, interferences from other elements and matrix effects tend to dominate. Preliminary chemical separations are often required. Maximum sensitivity must require optimisation for the matrix and the element(s) of interest, but at least SNO has primarily only one element to focus on, thorium.

Barrie Knox,
Department of Physics,
University of Oxford.
7th May 1990.

ATOMIC SPECTROMETRY UPDATES/ATOMIC SPECTROSCOPY GROUP

ROYAL SOCIETY OF CHEMISTRY

LASERS IN ATOMIC SPECTROSCOPY

29 March 1990

Lecture Theatre E
University of Surrey
Guildford

PROGRAMME

09.45 : Registration

10.10 : Chairman's Introduction

10.15 : "New directions for laser-enhanced ionization spectroscopy"
- G C Turk, NIST, Gaithersburg, USA

11.05 : Coffee

11.25 : "Applications of semi-conductor diode lasers in analytical atomic spectroscopy"
- K Niemax, ISAS, Dortmund, FRG

12.10 : "The fundamentals of ultratrace analysis using resonance ionisation mass spectrometry (RIMS)"
- K W D Ledingham, University of Glasgow

DEPT. OF PHYS & ASTRON,
GLASGOW G12 8QQ.

12.45 : LUNCH

14.00 : "Analytical atomic spectroscopy à la carte"
- K Kitagawa, Nagoya University, Japan

14.50 : "Photothermal techniques in analytical spectroscopy"
- R D Snook, DIAS, UMIST

15.30 : "Laser ablation particle production and analysis"
- C D Flint, M Thompson and S Chenery,
Birkbeck College, University of London

16.00 : Discussion

16.30 : Tea and disperse

NEW DIRECTIONS FOR LASER-ENHANCED IONIZATION SPECTROSCOPY

G C Turk (GREG TURK)

National Institute of Standards and Technology,
Gaithersburg, MD, USA

Laser-enhanced ionization (LEI) spectroscopy has been developed as a method for trace metal analysis in the flame, but recent research has progressed in a number of new directions. These include new atom reservoirs, molecular flame spectrometry, and new combinations of LEI with liquid chromatography and laser-induced fluorescence.

Many atomic analytical methodologies have largely abandoned the flame for higher temperature electrical plasmas, notably the ICP. Such plasmas have properties which would also be beneficial to LEI, but the high electron number density and radio-frequency interference of the ICP make LEI detection very difficult. We have demonstrated an approach to performing LEI measurement in a power-modulated ICP. The power to the ICP is cut for a brief period before the firing of the pulsed laser, resulting in lower background electron concentrations and the elimination of radio-frequency interference.

Molecular spectroscopy in flames for chemical analysis has not been a very active field of research in recent years, but new laser-beam detection procedures present new possibilities. We have developed a method for the determination of phosphorus based upon multiphoton ionization of phosphorus monoxide in the air-acetylene flame.

It is well recognized that the combination of atomic spectroscopic detection with liquid chromatography yields a powerful measurement capability for metal speciation. Trace concentrations and dispersion of the sample into the chromatographic mobile phase require very high sensitivity from the atomic spectroscopic detector. LEI has been utilized as a tin-selective detector for the determination of tributyltin in estuarine sediments.

Laser-induced fluorescence (LIF) and LEI differ greatly in the manner in which they detect a response to the laser-excitation of atoms, but this excitation process is identical for the two methods. The two measurements can be performed simultaneously with the same laser in the same flame, and such measurements yield some unique information. We have studied the correlation between noise in LEI and LIF, and have demonstrated a procedure which utilizes LIF for the measurement of spectral background interference in LEI spectrometry.

This talk will include a brief summary of the fundamental aspects of LEI for trace analysis, and a description of research performed at NIST in these various new directions.

USES A NEODYMIUM LASER TO PUMP 2 DYE LASERS (TUNABLE FOR MAX. OUTPUT) LASER PULSE IS ~ 5nS LONG. SENSITIVITY CLAIMED AS FROM 1 TO 1000 PARTS PER TRILLION (?)

INTERFERENCE FROM ALKALI METALS, e.g. WING OF SODIUM LINE INTERFERES WITH NICKEL DETERMINATION. BY USING LIF A CORRECTION CAN BE MADE FOR THIS.

APPLICATIONS OF SEMI-CONDUCTOR DIODE LASERS IN ANALYTICAL ATOMIC SPECTROSCOPY

K Niemax

Institute for Spectrochemistry and Applied Spectroscopy (ISAS),
Dortmund, Federal Republic of Germany

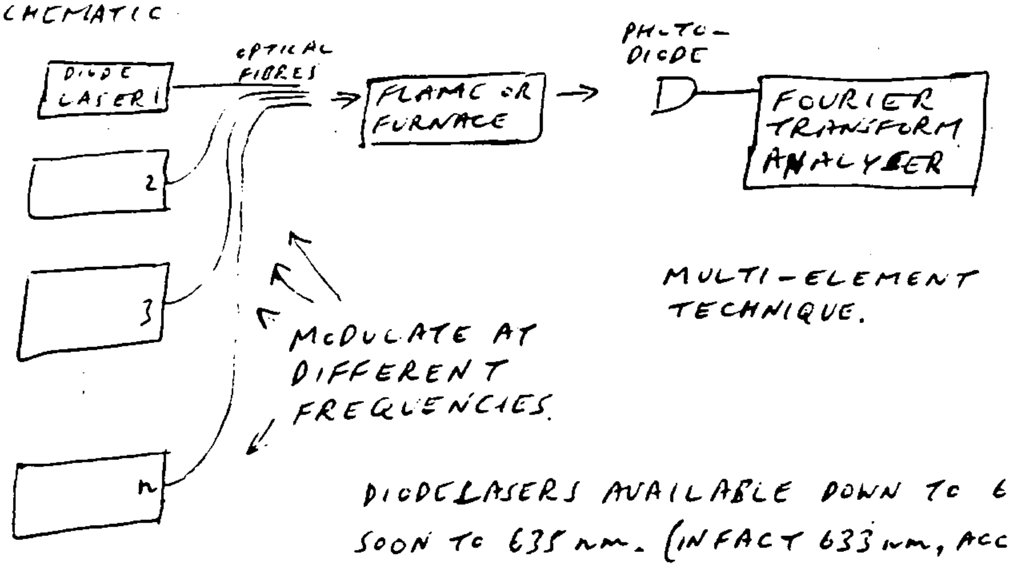
The acceptance of the powerful laser spectroscopic methods for element analysis by the community of analytical chemists is strongly dependent on the availability of simple, compact and inexpensive tunable lasers which allow multi-element analysis. Semi-conductor diode lasers are such spectroscopic devices. They are small and easy-to-operate radiation sources with excellent spectroscopic properties. In particular, the fast and reproducible tunability of the laser wavelength by the change of the diode current is of practical interest in analytical spectroscopy. If second harmonic generation of diode laser radiation in non-linear media is included, the wavelengths of commercially available diode lasers are already reaching the uv spectral range. New attempts and trends in measuring the wave-length, narrowing the spectral widths and increasing the power of semi-conductor diode laser devices will be discussed.

DYE LASER ARE LARGE, EXPENSIVE, COMPLICATED, SHORT-LIVED.
DIODE LASERS ARE SMALL, CHEAP (~$10), SIMPLE TO USE, LONG-LIVED.
THEY ARE TUNABLE BY a) CURRENT b) TEMPERATURE.

~30 GHz/°C and ~8 GHz/mA

TUNED BY ADJUSTING TEMPERATURE, STABILISING IT TO <0.01°C, AND ADJUSTING CURRENT FOR FAST TUNING (CAN BE COMPUTER-CONTROLLED). PELTIER ELEMENT USED, COUPLED TO A WATER-COOLED COPPER BLOCK.

SCHEMATIC



MULTI-ELEMENT TECHNIQUE.

WAVELENGTH FOR Th IS 371.94 nm.

DIODE LASERS AVAILABLE DOWN TO 645 nm, SOON TO 635 nm. (IN FACT 633 nm, ACCORDING TO NEW SCIENTIST, 31/3/90, p.35). ONLY Ba AND THE ALKALI METALS ARE COVERED BY THIS RANGE, BUT FREQUENCY DOUBLING ALLOW MOST ELEMENTS TO BE MEASURED.

THE FUNDAMENTALS OF ULTRATRACE ANALYSIS USING RESONANCE IONISATION MASS SPECTROMETRY (RIMS)

K W D Ledingham (KEN LEDINGHAM)

Department of Physics and Astronomy, University of Glasgow, G12 8QQ

Resonant Ionisation Mass Spectroscopy is a unique, ultra sensitive analytical technique which can detect down to the level of a few atoms or molecules. It can be used for any sample, solid, liquid or gas, stable or radioactive.

If the sample is a solid then an analysis consists of three steps:

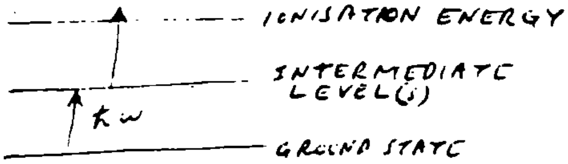
1) gasification by ion sputtering or laser ablation;
2) the neutral atoms or molecules are then resonantly ionised by one or more pulsed laser beams;
3) the ions created are mass analysed normally using a time of flight mass spectrometer.

Each of these steps will be described in detail, followed by typical results and limits of sensitivity using a reflectron TOF mass spectrometer system.

Applications of RIMS will be discussed particularly in:

a) profiling of quantum well structures in III/V semiconductor materials;
b) detection of small quantities of biomolecules and amino acids in supersonic jets;
c) carbon cluster formation in the laser ablation process;
d) initial results will be presented on resonant laser ablation.

RESONANT IONISATION BY 2-PHOTON OR 3-PHOTON PROCESSES CAN BE EXTREMELY SELECTIVE.



ANALYTICAL ATOMIC SPECTROSCOPY à La Carte

K Kitagawa

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Several aspects of analytical chemistry and analytical atomic spectroscopy will be presented in conjunction with "Analytical Sciences", the research topics of the lecturer's group and the Japanese societies associated with Analytical Chemistry.

La Carte 1: A Viewpoint on Analytical Chemistry and Analytical Atomic Spectroscopy

The lecturer, an analytical chemist (?), is sometimes puzzled when trying to extend the study of analytical atomic spectroscopy: on which aspect, theoretical (principle) or technological (instrumentation) or practical (application connected with the social demands), should the emphasis be placed? A discussion will be given with reference to the trends in Japan, "Diffusion of Analytical Chemistry to the Analytical Sciences".

La Carte 2: Some Topics of the Lecturer's Research Group

- Atomic Magneto-Optical Rotation (AMOR) using the Faraday effect
- A Separative Column Atomizer (SCA) or Atomic Gas Chromatograph
- A Super High Speed Scanning Spectrometer
- Correction of the Physical Interference in a Nebulizer using the Fraunhofer Diffraction of Laser Radiation
- An hf Capacitive Plasma with a Hot Cup or Thermal Atomizer in an hf Plasma

La Carte 3: The Chemical Society of Japan, associated with Analytical Chemistry and ICAS '91, Japan

Three societies, the Japan Society for Analytical Chemistry (JSAC), the Chemical Society of Japan (CSJ) and the Spectroscopical Society of Japan (SSJ), together with their journals and meetings, will be introduced briefly. In addition, arrangements for the International Congress on Analytical Sciences, which will be held in 1991 in Tokyo (ICAS '91), and the Joint and Satellite Conference on new approaches in trace element analysis by atomic spectroscopy, Kitami, Japan, will be announced.

TOWARDS END OF TALK DESCRIBED MEASUREMENTS OF Cu, Ni, ETC, AT 10ppb LEVEL. BY ANOTHER METHOD A FEW TENS OF pg OF Cd COULD BE DETECTED IN A VERY SMALL SAMPLE, ~5μl.

MAIN PART OF TALK WAS ABOUT THE 3 JAPANESE SOCIETIES AND THE CONFERENCES THEY ARE PLANNING IN AUG/SEPT 1991.

PHOTOTHERMAL TECHNIQUES IN ANALYTICAL SPECTROSCOPY

R D Snook (DICK SNOOK)

DIAS, UMIST, P O Box 88, Manchester M60 1QD

In this paper the development of photothermal spectroscopy and its analytical applications will be described. Photothermal spectroscopy is a term used to describe a family of techniques which includes photoacoustic spectroscopy, thermal lens spectroscopy and photothermal beam deflection spectroscopy. In the work being pursued at UMIST most emphasis is placed upon the development of the two latter techniques for spectrometric analyses.

In thermal lens spectrometry (1) a laser is used to excite chromophores in solution. Non-radiative decay routes of the excited chromophore leads to local heating of the solvent which in turn leads to a refractive index change in the beam/sample interaction volume. For most solvents the change in refractive index with temperature is negative (−dn/dT) which causes the solution to behave as a diverging lens. For a gaussian beam profile this causes a reduction in beam intensity at the beam centre which can be monitored in the far field of the thermal lens using a pinhole aperture and photomultiplier detector. The thermal lens signal, θ is related to the absorbance of the chromophore through the following equation

$$\theta = \frac{-2.303\,P(dn/dT)A}{\lambda k}$$

The sensitivity of the technique is therefore power dependent, P being the power of the pump beam, λ the laser wavelength and k the thermal conductivity of the solution. The technique can be used to gain the same information as conventional UV/visible spectrophotometry but limits of detection are improved by as much as three orders of magnitude because of the power enhancement factor. The determination of U(VI) and Cu(II) in solution will be described using a novel mode-mismatched two beam thermal lens spectrometer.

The thermal lens technique also allows the thermal power absorbed to be measured. The Quantum efficiency Qf of fluorescent molecular species in solution can therefore be measured using the thermal lens technique (2) as the total absorbed power (excitation and thermal power) can be quantified.

This method will be described and results for the quantum efficiency of sodium fluorescein will be presented.

Photothermal beam deflection spectrometry is analogous to photoacoustic spectrometry (PAS) in that it relies on the conversion of absorbed radiation to heat in a solid sample. If the pump beam is modulated then the resulting heat flow in the sample is represented as a thermal wave, which can be quantified above the surface of the sample in a contacting gas medium. In PAS the detector is a closed microphone cell but this presents limitations for many sample types. In photothermal beam deflection spectrometry a second laser beam passing just above the plane of the sample is used for detection with the advantage that "open" samples can be analysed. The thermal wave causes a periodic change in refractive index of the contacting gas which deflects the beam. The magnitude and phase relationship with the modulated laser beam can be determined using a position sensitive detector and lock-in amplifier/phase sensitive detector combination. In this paper a model and experiments proof for probe beam deflection will be presented. Application of the technique to the determination of Si dopant levels in GaAS semi-conductors will be presented and applications to membrane diffusion studies will be discussed.

References

1. Jun Shen and R D Snook, 1989, Anal. Proc., 26, 403.
2. Jun Shen and R D Snook, 1989, Chem. Phys. Letter, 155, 583.

FOR Cu CLAIMS LOD OF $2{\cdot}1 \times 10^{-13}$ g (5×10^{-8} M SOLUTION)
FOR Cu COMPLEXED WITH EDTA LOD OF $3{\cdot}35 \times 10^{-14}$ g CLAIMED.

THE PRODUCTION OF PARTICLES BY LASER ABLATION AND THEIR SERIAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY

S Chenery, C D Flint and M Thompson (GIVEN BY SIMON CHENERY)

Birkbeck College, University of London

The production of individual micron sized particles by the laser ablation (LA) of test materials has been observed by two research groups (1,2). It has been proposed by these groups that the particles form a major proportion of material analysed by LA-ICP-AES and LA-ICP-MS systems. The individual detection of the particles by both LA-ICP-AES and -MS was demonstrated by Thompson *et al.*(3). Thompson proposed that signal analysis of a large number of individual particles on a millisecond scale would provide superior detection limits compared to simple signal integration over several seconds. Superior detection limits would be the result of avoiding collecting background signal between the arrival of any two particles. A suitably sophisticated data collection and analysis system for particles is as yet unavailable in commercial ICP-AES and -MS instruments. This presentation will describe two threads of research. The first is the background study to the development of a LA-ICP-AES system, designed specifically for the analysis of single particles. The second is the chemical characterisation of the particles produced by laser ablation using electron probe microanalysis (EPMA).

To investigate the effect of both laser and ICP parameters on the production and analysis of single particles, a dual channel digital storage oscilloscope (DSO) was connected to two photomultipliers on a polychromator ICP-AES. Particles were produced by laser ablation and the resultant DSO traces photographed. The 694nm ruby laser's input energy and Q-switching were altered and the ICP-AES response observed. The Q-switching controls the laser's peak power. The input power and the injector gas flow rate of the ICP- AES were also varied and the response observed. It was concluded that variations in laser parameters affected the number of particles produced rather than their size. The ICP-AES parameters were found to be very tolerant of particle introduction, input power could be reduced to a very low level without serious loss of response and low injector gas flow rates showed little loss in the number of particles analysed.

The second area of interest is chemical characterisation of the particles from different types of test material such a stainless steel, iron sulphide and ferro-magnesium silicate. The particles produced by 3 lasers of different wavelengths and peak powers have been captured on membrane filters. Several hundred particles, in each case, were then subjected to EPMA. Their analyses, if possible, were compared to similar sized fragments produced by crushing. The range of measured chemical compositions suggests a complicated origin involving both melting and vaporisation of the test material. The unusual composition range of particles produced by laser ablation also suggests it may be some time before the origin of matrix effects associated with LA-ICP-AES and -MS are resolved. The development of the new LA-ICP-AES single particle analysis system should prove an ideal tool to investigate these matrix effects.

1. Chenery, S *et al.*, Anal. Proc., 1988, 25, 68.
2. Arrowsmith, P and Hughes, S K, Appl. Spectrosc., 1988, 42, 1231.
3. Thompson, M *et al.*, J. Anal. At. Spectrom., 1988, 3, 1133.

ATOMIC SPECTROMETRY UPDATES/ATOMIC SPECTROSCOPY GROUP

ROYAL SOCIETY OF CHEMISTRY

LASERS IN ATOMIC SPECTROSCOPY

LIST OF PARTICIPANTS

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Dr J S Crighton	B P Research
Mr S M Culshaw	DIAS, UMIST
Mr S R Davies	University of York
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Mr P S Goodall	Polytechnic South West
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Mr H W Handley	Polytechnic South West
Mr J H D Hartley	Polytechnic South West
Mr M A Hassan	University College, Swansea
Dr D A Hickman	Metropolitan Police
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Dr K W D Ledingham	University of Glasgow
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Dr M Thomsen	Perkin-Elmer Ltd
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Dr G C Turk	NIST, Gaithersburg
Dr J Tushingham	AEA Technology
Prof J F Tyson	University of Massachusetts
Dr A M Ure	University of Strathclyde
Dr P Van de Weyer	Philips Research Laboratories
Dr A A Van Heuzen	Shell Research, Amsterdam
Dr J G Williams	Royal Holloway and Bedford New College
Mr H S Wise	Wantage

The Fifth Biennial National Atomic Spectroscopy Symposium

will be held at the

University of Technology, Loughborough

5th BNASS

18 – 20 July 1990 (WED, THURS, FRI)

The symposium will provide a forum where interesting and useful applications of atomic spectroscopy can be reported and discussed. In addition to plenary, invited and submitted lectures, a particular feature of the meeting will be the presentation of posters. There will also be an exhibition and a social program for delegates and their guests.

This meeting is organised by the Atomic Spectroscopy Group, Analytical Division of the Royal Society of Chemistry.

Further information can be obtained from the Chairman of the organising committee:
Dr D A Hickman, The Metropolitan Police Forensic Science Laboratory, 109 Lambeth Road, London SE1 7LP.

REGISTRATION FORM FROM: (TO BE RETURNED BY 31st MAY)

Dr. STEVE HILL, DEPARTMENT OF ENVIRONMENTAL SCIENCE,
POLYTECHNIC SOUTH WEST, DRAKE CIRCUS, PLYMOUTH, DEVON, PL4 8AA.

FEE: RCS MEMBER £160
NON-MEMBER £200

36th Canadian Spectroscopy Conference
August 1–3, 1990, Brock University, St. Catharines, Ontario, Canada

Contributions from all areas of atomic and molecular spectroscopy are invited for this meeting. The following sessions are being organised: analytical atomic spectroscopy; inductively coupled plasma mass spectrometry; applications of Fourier transform infrared spectrometry; liquid chromatography - mass spectroscopy—advances; spectroscopic methods in archaeometry; applied NMR; industrial applications of spectroscopy; environmental applications of spectroscopy; advances in mass spectrometry; and new techniques for ultra-trace determinations.

Authors should submit approximately 250-word abstracts, in duplicate, before March 1, 1990. In case of multiple authorship, underline the name of the speaker.

Abstracts and programme enquiries should be sent to: Ian D. Brindle, Chemistry Department, Brock University, St. Catharines, Ontario, Canada L2S 3A1; telephone (416) 688 5544, extn. 3545. For exhibition enquiries contact: Jack M. Miller, Chemistry Department, Brock University, St. Catharines, Ontario, Canada L2S 3A1; telephone (416) 688 5544, extn. 3402.

JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY, AUGUST 1989, VOL. 4

Effect of Ascorbic Acid on the Appearance Temperature of Lead in Graphite Furnace Atomic Absorption Spectrometry

G. F. R. Gilchrist, C. L. Chakrabarti* and J. P. Byrne†
Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, Ottawa, Ontario K1S 5B6, Canada

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A thermodynamic (gas phase) equilibrium model of atomisation has been used to explain the shift of the appearance temperature of the Pb atomic absorption signal to a lower value when ascorbic acid is used as a matrix modifier. Experimental results of the effect of gas-phase composition on the appearance temperature of the Pb atomic absorption signal are presented. The partial pressure of H_2 was determined at various temperatures during the ashing and the atomisation cycle. The partial pressure of CO, CO_2 and CH_4 were found to be very low for the tube wall heating rate of 1.7 K ms^{-1}; CO was found to be present in appreciable amounts for the tube wall heating rate of 1.5 K ms^{-1}. The results are consistent with the hypothesis that H_2 and CO released by the pyrolysis of ascorbic acid decrease the partial pressure of O_2 in the furnace and thereby cause the equilibrium position of the reaction $PbO_{(g)} \rightleftharpoons Pb_{(g)} + \frac{1}{2} O_2$ to shift to the right, favouring production of more $Pb_{(g)}$, which results in a lowering of the appearance temperature of the Pb atomic absorption signal in agreement with the equilibrium model.

Keywords: *Graphite furnace atomic absorption spectrometry; lead; matrix modifier; thermodynamic equilibrium model*

A number of workers[1–4] have reported that some organic compounds, including ascorbic acid, are effective matrix modifiers for graphite furnace atomic absorption spectrometry (GFAAS). McLaren and Wheeler[1] have shown that the addition of 1% *m/V* ascorbic acid causes the appearance of a second peak in the atomic absorption (AA) signal of Pb; they have also shown that the Pb AA signal is shifted to a lower appearance temperature if ascorbic acid is added to the Pb (in aqueous solution). Regan and Warren[2] have shown that ascorbic acid causes a decrease in the appearance temperature of Pb and that the double peaks observed by McLaren and Wheeler[1] can be eliminated by using a sufficiently large amount of ascorbic acid. Another interesting observation made by Regan and Warren[2] is that in the presence of 1% *m/V* ascorbic acid the maximum atomisation temperature of Pb can be reduced from 2100 to 1300 °C without a decrease in the peak-height absorbance signal.

Tominaga and Umezaki[3] have shown that the addition of 0.05% *m/V* ascorbic acid causes appearance of double peaks and a shift to a lower appearance temperature of Pb, whereas addition of 5% *m/V* ascorbic acid causes appearance of a single peak and a similar shift to a lower appearance temperature of Pb. They[3] have also shown that in the presence of ascorbic acid the peaks of the AA signals of Mn and Sn are shifted to higher temperatures. To date these results have been inadequately explained, although Sturgeon and Berman[4] have suggested that pyrolysed ascorbic acid forms active centres, which enhance the rate of scavenging of oxygen and cause a decrease in the appearance temperature of volatile metals. These workers reported that the addition of 1% *m/V* ascorbic acid causes the appearance temperature of Pb to decrease from 1045 to 955 K when Ar is used as the purge gas. They[4] have also indicated that ascorbic acid causes the appearance temperature of Pb to decrease from 1160 to 960 K when Ar containing 0.517% *V/V* O_2 is used as the purge gas.

The effect of gases added to the purge gas in GFAAS has been the subject of a number of investigations.[4–8] Steiner and Kramer[5] have reported that the addition of a combination of H_2, N_2, O_2 or CH_4 to the furnace gas during the ashing or the atomisation cycle causes an enhancement in the absorbance signal and a greater linearity in the analytical calibration graphs of Pb and Cd in bovine liver samples. Guerrieri *et al.*[6] cited an example of Pb, atomised with H_2 as the purge gas, giving an appearance temperature that is 500 K lower than that when Ar is used as the purge gas. Byrne *et al.*[7] have shown that the addition of $O_{2(g)}$ to the Ar purge gas causes an increase in the appearance temperatures of Pb, Sn and Si. Both Sn and Si have appearance temperatures much higher than the temperature at which O_2 is desorbed from the graphite surface.[9] It is therefore not very likely that the reported[7] shifts in the appearance temperatures of these elements are due to surface reactions involving chemisorbed oxygen. Frech *et al.*[8] found that Pb, Bi and Cr, which are considered to be atomised by thermal decomposition of their condensed-phase or gaseous oxides, show substantial shifts to lower appearance temperatures when CO is added to the Ar purge gas. These workers[8] have also reported that on addition of CO to the Ar purge gas, changes in the activation energy for atomisation of the above elements have been observed. However, neither the appearance temperature nor the activation energy for atomisation of Cu is affected by the addition of CO to the Ar purge gas.[8]

Theory

Assuming the equilibrium model proposed by Byrne *et al.*[7] to be applicable to the present study, the shift of the Pb AA signal to a lower temperature may be explained in terms of a shift to the right in the equilibrium of the following reaction:

$$PbO_{(g)} \rightleftharpoons Pb_{(g)} + \tfrac{1}{2} O_{2(g)} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Byrne *et al.*[7] have shown that the amount of $O_{2(g)}$ in the purge gas strongly influences the appearance temperature of Pb. In order for this model to be applicable to the atom formation process, the equilibrium shown by equation (1) must be established in the gas phase. As discussed by Byrne *et al.*,[7] such a gas-phase equilibrium can be established only if PbO molecules exist in the gas phase at the appearance temperature of Pb and the reaction kinetics are sufficiently rapid to establish equilibrium within the residence time of Pb atoms within the furnace. Evidence that PbO molecules exist in the gas phase at the appearance temperature of Pb can be found in the literature: the vaporisation of Pb in GFAAS reported by Sturgeon *et al.*[10]; and Bass and Holcombe[11,12] have reported

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Graphite Furnace Atomic Absorption Spectrometric Determination of Nickel at Sub-ng g^{-1} Levels in Marine Samples by Carbonyl Generation With *In Situ* Pre-concentration*

Ralph E. Sturgeon, Scott N. Willie and Shier S. Berman
Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R9, Canada

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Reduction of Ni^{II} in solution by addition of BH_4^- and its carbonylation in a stream of CO - Ar serves to transfer the volatile $Ni(CO)_4$ from a generation cell to a pre-heated graphite furnace where it undergoes decomposition and deposition at $T > 500\,°C$. Subsequent atomisation at $T > 2700$ K and measurement of the atomic absorption serves to quantify Ni in test samples by direct comparison with signals derived from identically treated solutions of standards. The system is *ca.* 80% efficient and is characterised by a concentration detection limit (3σ) of 4 ng l^{-1}, based on a 10-ml test sample. Results are presented for the analyses of several natural water and biological reference materials.

Keywords: *Graphite furnace; atomic absorption spectrometry; nickel carbonyl;* in situ *concentration*

Nickel has been the subject of a number of investigations as a result of its environmental, toxicological and physiological importance. The most common method of analysis has been graphite furnace atomic absorption spectrometry (GFAAS). The sub-µg g^{-1} concentrations of Ni in many materials of environmental interest precludes the conventional direct determination of this element, necessitating the use of pre-concentration and/or matrix separation techniques.

As an alternative to this approach, several workers have examined the feasibility of utilising the high volatility and ease of formation of $Ni(CO)_4$ to effect a matrix separation and concentration of Ni prior to determination.[1-3] This technique can be rapid, relatively free of contamination that could be introduced through reagents or manipulation, and not subject to severe interferences.

Vijan[1] was the first to exploit the analytical applications of $Ni(CO)_4$ for analytical purposes and reported some feasibility studies which revealed the technique to be sensitive (19 pg per 0.0044 A) when coupled to a heated quartz cell (800 °C) for atomisation.

Lee[2] was the first to apply the technique to real samples and determined Ni in sea water. The carbonyl was first concentrated on silanised glass-wool immersed in liquid N_2 and the contents then warmed and passed as a vapour plug into a heated quartz tube supporting an H_2 - air flame. An absolute detection limit of 0.2 ng was achieved (limited entirely by the blank) using 20-ml sample volumes. This permits a relative detection limit of 0.01 ng ml^{-1}. An absolute sensitivity of 50 pg was reported. A more extensive application of $Ni(CO)_4$ generation to environmental analyses was undertaken by Alary *et al.*[3] These workers passed the generated carbonyl directly into a heated quartz cell (950 °C). A number of environmental samples, biological fluids and reference steel samples were analysed to test the validity of the method. A 10-ng limit of detection was reported.

Recently, Drews *et al.*[4] utilised the rapid kinetics of the carbonylation reaction to achieve detection limits of 100 pg (1 ng ml^{-1} relative) for the determination of Ni in urine samples. A flow injection system coupled to a microwave-induced plasma system permitted 120 measurements per hour.

In the present study, a number of environmental materials have been analysed for their Ni content using CO to generate the carbonyl and a heated graphite furnace to collect and subsequently atomise the analyte. This procedure is similar to that used for the *in situ* collection of volatile hydrides[5] and permits large pre-concentration factors (500-fold) to be attained in 2–3 min with a minimum of sample manipulation.

Experimental

Instrumentation

Analytical absorption measurements were made using a Perkin-Elmer (Norwalk, CT, USA) Model 5000 system fitted with an HGA-500 graphite furnace and Zeeman-effect background correction. The injection hole in the pyrolytic graphite coated graphite tube was increased to about 2.4 mm to accommodate the quartz transfer line.

Time-resolved absorbance and temperature measurements in the graphite furnace were obtained with an HGA-2200 furnace mounted in a modified Varian Techtron (Melbourne, Australia) Model AA-5 spectrometer.[6] A Series 1100 optical pyrometer (Ircon, Niles, Il, USA) was sighted through the sample introduction hole in the graphite tube and blackbody conditions were assumed.

Auger electron spectroscopy was used to characterise the sample residue in the furnace. A Perkin-Elmer Physical Electronics Industries Scanning Auger Microprobe Model 590 was used for this purpose.

Nickel carbonyl was generated in a custom made Pyrex cell[5] into which a 1% *m/V* solution of sodium tetrahydroborate(III) was metered using a peristaltic pump. A schematic diagram of the experimental set-up is shown in Fig. 1. The main valve and three-way valve (PTFE stopcocks in glass bodies) were manually operated and all gas lines were

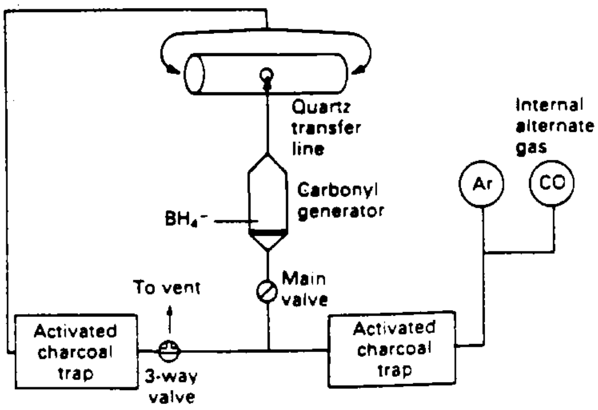

Fig. 1. Schematic diagram of the experimental system

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Analysis of a Rhenium - Osmium Solid-solution Spike by Inductively Coupled Plasma Mass Spectrometry[*]

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The rhenium - osmium decay scheme (^{187}Re → ^{187}Os) offers a unique opportunity to investigate the genesis of, and directly date, ultramafic rock, sulphide and platinum ore deposits. Inductively coupled plasma mass spectrometry (ICP-MS) is a viable method for Os isotopic analysis as it provides the high temperatures necessary to ionise Os. The sample can be introduced into the ICP mass spectrometer either by conventional nebulisation or by distillation using an Os "generator." Generator-mode analysis is superior to nebulisation because (i) the total number of counts is two orders of magnitude higher for a given sample size and (ii) Os oxidises readily to volatile OsO_4, which has a boiling-point lower than most Re compounds, so that Os can be efficiently separated from ^{187}Re. The importance of Os loss during sample preparation was minimised by combining the sample powder with a powdered Re - Os isotopic spike prior to any chemical treatment. The spike is in a nickel sulphide matrix and was made by a thioacetamide co-precipitation of Os, Re and Ni followed by a fire assay. The ^{190}Os/^{192}Os ratio in this preparation is 51.5 ± 0.9, the ^{187}Os/^{188}Os ratio is 0.063 ± 0.006 and the ^{185}Re/^{187}Re ratio is 17.04 ± 0.41. These values are within the error limits quoted by the Oak Ridge National Laboratory and Techsnabexport, the suppliers of the metallic spikes. Parameters that significantly influence the Os analyses include the oxidising agent and the run temperature. The oxidising agent H_5IO_6 is preferred to H_2O_2 or HNO_3 as it has the highest electrode potential, provides a prolonged, consistent reaction and is more stable when stored. Chilling the sample and the H_5IO_6, initially retards uncontrolled OsO_4 emission. Heat applied later in the run releases OsO_4 and helps maintain a high count rate. Thus, OsO_4 can be generated in a steady, controllable and reproducible manner.

Keywords: *Inductively coupled plasma mass spectrometry; distillation; isotopic analysis; solid-solution spike; osmium and rhenium analysis*

Osmium and rhenium are heavy transition metal elements with relative atomic masses spanning the range 184–192. Osmium has seven naturally occurring isotopes, while Re has two, one of which (^{187}Re) is radioactive and decays via low energy β decay to ^{187}Os. The half-life is 4.35 × 10^{10} years, based on direct counting experiments.[1] This is in general agreement with the decay constants derived from Re - Os isochrons determined on iron meteorites[2] and molybdenites of known age.[3] Osmium is a platinum group element (PGE). In contrast, Re is similar to molybdenum or tungsten. This difference in chemical affinity means that there is a wide range of Re/Os in nature. Hence this elemental pair is potentially useful as a geochronometer or isotopic tracer that can contribute to meteorite studies, mantle evolution, Cretaceous - Tertiary boundary problems and the direct dating of many types of ore deposits (platinum, nickel, chromium, molybdenum and copper).

Although potentially a powerful geochemical tracer, the Re - Os system has not been widely used. The very high ionisation potential of Os (8.5 V) precludes Os determination by thermal ionisation mass spectrometry (TIMS). By comparison, Rb, Sr, Sm and Nd determinations by TIMS on Re filaments, have ionisation potentials of less than 6 V. Osmium and Re are among the least abundant naturally occurring stable elements in crustal rocks, even when concentrated in platinum or molybdenum deposits. Furthermore, ^{187}Os makes up only 1–2% of the total Os. Thus, as pointed out by Dickin *et al.*,[4] precise Os isotopic work is limited by counting statistics. There is isobaric overlap between Os and Re at 187 u, Os and W at 184 and 186 u, and Os and Pt at 190 and 192 u. Fortunately, Re interference can be monitored using ^{185}Re.

Other analytical problems include the easy oxidation of Os to OsO_4. The low boiling-point (130 °C) of this gas means that Os is readily lost from oxidising solutions. Finally, Os bearing minerals are alloys and tend to be insoluble in inorganic acids. These minerals are often unevenly distributed in geological materials, thus producing a significant "nugget" effect. Although this is not an insurmountable problem, pre-concentration or separation techniques such as fire assay, alkali fusion, precipitation or ion-exchange chromatography are necessary in order to analyse such materials. Techniques used for Re - Os isotopic analyses include resonance ion mass spectrometry (RIMS),[5] secondary ion mass spectrometry (SIMS),[2] spark source mass spectrometry (SSMS),[6] accelerator mass spectrometry (AMS),[7] laser ablation mass spectrometry (LAMMA) and inductively coupled plasma mass spectrometry (ICP-MS).[4,8–10] Analyses of Re - Os isotopes could also be carried out using glow discharge mass spectrometry (GDMS), but as yet this has not been attempted.

Experimental

Equipment

Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry is an appropriate method for Re - Os isotopic analyses as the high temperatures of the plasma (>6000 °C) ionise 78% of the Os and 93% of the Re.[11] For this study, a Sciex Elan Model 250 ICP mass spectrometer was used. Operating conditions invariant during this study are listed in Table 1. To facilitate the determination of Os, the Elan was modified so that the sample introduction devices (standard nebuliser or OsO_4 generator) were outside the top housing. Such a placement allows easy access to the generator for the determination of Os and readily facilitates changing sampling devices between the analytical techniques. This arrangement also has the added advantage of temperature stability during generator and nebuliser analyses. Plasma conditions can be monitored by an infrared-sensitive phototransistor mounted on the frame of

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Mass Spectrometric Determination of the Temperature of an Argon Inductively Coupled Plasma From the Formation of the Singly Charged Monoxide Rare Earths and their Known Dissociation Energies

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The effect of inductively coupled plasma (ICP) parameters on plasma temperatures was studied by mass spectrometry using a commercially available SCIEX inductively coupled plasma mass spectrometer. Parameters varied include nebuliser gas flow, auxiliary gas flow, r.f. power and liquid sample uptake. The plasma temperatures were determined from the energy of formation of the singly positive charged monoxide ions from the singly charged positive metal ion and oxygen. As the nebuliser gas flow was changed, the measured plasma temperature varied from 12 400 (nebuliser gas flow 0.6 l min^{-1}) to 5100 K (nebuliser gas flow 1.4 l min^{-1}). An increase in temperature from 9000 to 12 700 K was observed as the power was increased from 1200 to 1500 W, or to 12 500 K when the auxiliary gas flow was decreased from 2.0 to 1.0 l min^{-1}. A decrease in the liquid sample uptake from 1.0 to 0.2 ml min^{-1} caused a temperature increase from 9000 to 11 500 K.

Keywords: *Inductively coupled plasma mass spectrometry; rare earth elements; plasma temperature singly positive charged ions; plasma temperature*

That a temperature can be determined from the energy of formation of the monopositive monoxide ion from the corresponding monopositive metal ion was reported by Douglas and French in 1986 where a temperature of 21 000 K was obtained.[1] and by our group in 1987 where a temperature of 10 100 K was determined.[2] A temperature has also been reported from the intensities of the singly and doubly charged ions.[3] There have been many reviews on the fundamental importance of the problem of determining ICP temperatures; important recent reviews of plasma temperature measurements were published in 1986[4] and in 1987.[5] These reviews describe the various methods for determining temperature and also the results obtained using optical emission methods. The various temperatures reported[5] vary from a low value of 2300 K to a high value of 52 000 K and, furthermore, show that the ICP is not in "local thermodynamic equilibrium" (LTE) as the various methods yield different temperatures. It is not the purpose of this paper to review the history of plasma temperature measurements and the significance of their determination to the understanding of fundamental processes taking place in the ICP; however it does show that a temperature determined from the formation of singly positive charged metal oxide molecular ions from singly positive charged metal ions and oxygen produces a meaningful temperature with particular relevance to the application of ICP-MS to applied analytical chemistry. This temperature may be indicative of processes taking place in the expansion jet of the mass spectrometer interface in addition to processes taking place in the plasma torch. The resulting temperature is the temperature that is of importance to mass spectroscopists in understanding the ICP-MS signals, setting up and aligning the instruments, and in obtaining satisfactory, meaningful and reproducible results. The rare earth oxide interferences, especially on Eu, Gd and Tb, are very important for the application of ICP-MS to geological samples and were the reason for this study being undertaken.

The effect of the ICP parameters (nebuliser, auxiliary and plasma gas flows and power) on ion signal intensity has been elucidated by Horlick *et al.*[6] Although all the parameters affected the ion signal intensity, the nebuliser gas flow was the most sensitive and was chosen as the independent variable in most of the results reported. Our group reported the effect of liquid sample uptake of the concentric nebuliser (controlled by a peristaltic pump) on the ion signal intensity.[7] Later the effect of the nebuliser gas flow on the rare earth ion and rare earth oxide ion intensities was demonstrated,[2] where following Horlick *et al.*[6] the nebuliser gas flow was used as the independent variable.

Theory

The equilibrium of the metal oxide monopositive ion with the monopositive metal ion and neutral oxygen can be given as

$$\mathrm{MO^+} \rightarrow \mathrm{M^+} + \mathrm{O}\text{: dissociation energy} = D$$
$$D = -RT\ln([\mathrm{M^+}][\mathrm{O}]/[\mathrm{MO^+}])$$

where R is the universal gas constant and T is the temperature. This equation can be rearranged to:

$$\mathrm{Log}\,([\mathrm{MO^+}]/[\mathrm{M^+}]) = D/[RT \times \ln(10)] + \text{constant}$$

graphically a plot of $y = \log([\mathrm{MO^+}]/[\mathrm{M^+}])$ *versus* $x = D$ gives a straight line:

$$y = \text{intercept} + \text{slope} \times D$$

where

$$\text{slope} = 1/[\ln(10) \times RT]$$

or

$$T = 1/[\ln(10) \times R \times \text{slope}]$$

The constant (intercept) is a function of the fugacity of oxygen and is constant for a set of elements determined at a given set of operating conditions.

A least-squares fit of the data $y = \log([\mathrm{MO^+}]/[\mathrm{M^+}])$ *versus* $x = D$ gives the slope and the error in this slope of the line from which the plasma temperature is calculated. In this study the standard simplifying assumptions of no error in x and the error in the y data, $\log([\mathrm{MO^+}]/[\mathrm{M^+}])$, is a constant was used and proved to be satisfactory. More elegant least-squares procedures which weigh either the y data or both x and y data were tried with no improvement. The lack of improvement with more sophisticated least-squares procedures will be shown to be due to the uncertainty in the bond dissociation energies used. The standard deviation determined from the