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SPARK SOURCE MASS SPECTROMETRY AND ATOMIC ABSORPTION SPECTROMETRY IN THE ANALYSIS OF HIGH PURITY MATERIALS

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Abstract - Spark source mass spectrometry (SSMS) and atomic absorption spectrometry (AAS) have played important roles as powerful analytical tools. Both these techniques have undergone significant improvements since the late fifties in instrumentation and methodology leading to their application in various branches of science and technology. These techniques can be regarded as complementary techniques in the analysis of high purity metals, semi-conductors and also non-conducting powders. SSMS is capable of analysing almost all elements at parts per billion levels, semi-quantitatively as a survey analysis and AAS can be employed to analyse for several elements with the required precision.

INTRODUCTION

Progress in materials science research, and the rapid growth of modern technology over the past three decades has led to the preparation and characterisation of a variety of high purity materials. Compositional characterisation of high purity materials is being carried out regularly by analysing for impurities at ppm-ppb levels. Examples are (i) analysis of semi-conductors for several atypical impurities, which influence their electrical properties, even at ppb levels and (ii) analysis of 4N to 6N purity zone-refined materials for all metallic impurities. Similar analyses are also required to identify one or more impurities as possible cause for the malfunctioning of material during applications.

Several analytical techniques[1] like emission spectrography, X-ray fluorescence spectroscopy, atomic absorption spectrophotometry, activation analysis and spark source mass spectrography are being employed. Ideally, the technique should have multielement capability with high sensitivity and specificity with minimum 'detection selectivity'. The above mentioned techniques, except spark source mass spectrography, meet one or two but not all the criteria listed above. Hence their application is restricted. It is generally accepted that SSMS is ideally suited for the survey analysis of 'almost all elements' in almost all matrices, though the results in the absence of extensive calibration of the photographic plate or electrical detection may be semi-quantitative in nature. The application of SSMS and AAS as complimentary techniques in the analysis of high purity materials, developed and produced at Chemistry Division, Bhabha Atomic Research Centre, Bombay and Special Materials Plant, Hyderabad, India, is described here.

Radio-frequency (RF) spark source mass spectrometer, having a Mattauch-Herzog geometry and photographic detector, is commonly employed to carry out the survey analysis of high purity materials because of the following significant advantages. RF spark ion source is capable of ionising metals and semi-conductors, non-conducting powders are briquetted with graphite. The 'ion cloud' is regarded as representative of the sample. The Mattauch-Herzog geometry reduces the energy spread of the ions, sorts out the ions according to their mass-to-charge ratios and focusses them on a plane, so that, mass lines from 7 to 252 can be recorded simultaneously. Q-2 photographic plates have a very large dynamic range and also act as a 'chemical amplifier' hence analysis of almost all elements at ppb and higher levels of concentration is possible. Ahearn[2] should be consulted for a comprehensive discussion on this

technique.

Flame atomic absorption spectrometry, a technique mostly used to determine metal ion concentrations in solution, is capable of analysing about 65 elements, 30 elements at sensitivities at about 0.05 $\mu g\ ml^{-1}$ (1% absorption). Hydride generation and electro-thermal atomisation, wherever applicable, improve the sensitivity by a factor 100-1000. Pre-concentration is necessary where inter-element interferences are severe and is desirable where sensitivity is inadequate. Robinson[3], Slavin[4], Kirkbright and Sargent[5] should be consulted for comprehensive discussions concerning theory, methodology and applications.

ANALYTICAL PROCEDURE

Metals and semi-conductors are machined to $\backsim$ 2 cm long rods of 0.03-0.05 cm^2 cross-section, chemically etched and mounted as electrodes in the ion source of the mass spectrometer. Non-conducting powders are mixed with high purity graphite, briquetted and similarly mounted. Sparking conditions like pulse length, pulse repetition rate and spark voltage are kept constant during all exposures. The experimental operating parameters used with the Nuclides Graf 3S spark source mass spectrometer are given in Table 1.

TABLE 1. Operating parameters used for spark source mass spectrometric analysis

Source pressure (during sparking)	$1\text{-}2 \times 10^{-6}$ torr
Electrostatic analyser pressure	4×10^{-8} torr
Magnetic analyser pressure (with LN_2 cryogenic cooling)	2×10^{-8} torr
Spark voltage	25-30 KV
Pulse length	10 μ sec
Pulse repetition rate	1000 sec^{-1}
Accelerating voltage	15 KV
Magnetic field	13000 gauss

The electrodes are presparked to remove surface layers. Thirteen exposures are recorded in the range of 10^{-13} to 10^{-7} C, increasing in steps of $\sqrt{10}$. Magee and Harrison[6] showed that the sensitivity for several elements are markedly affected due to the variation in the spark gap during sparking. Several manufacturers now supply an automatic spark gap control unit, with or without an electrode vibrator. The spark gap can also be monitored using a small piece of wire as an antenna and connecting it to an oscilloscope capable of measuring 1MHz. The radio-frequency voltage picked up by the wire (usually 1-2V) is displayed on the Oscilloscope screen. This spark gap can be adjusted manually by initiating the spark at a particular voltage.

Q-2 plates are developed using the latent image developer, described by Cavard[7]. Semi-quantitative and quantitative evaluation of spectral lines on the plate are carried out by visual and micro-densitometric methods respectively. In both these methods, the most important assumption is that the same number of atoms produce similar blackening. In the visual method, the exposures necessary to produce a just detectable line for matrix and impurity element lines are read from the plate and the concentration of the impurity Ci is computed from the relation

$$Ci = \frac{Es}{Ei} \cdot \frac{X}{100} \cdot \frac{Is}{Ii} \cdot 10^6 \text{ ppm atomic}$$

where, Es and Ei are the exposures required to form just detectable lines of matrix and impurity isotopes respectively, Is and Ii are the natural abundances of the isotopes of matrix and impurity elements respectively and X is the concentration of the matrix element in percentage. In the microdensitometric method, optical density (O. D.) of the lines, for matrix and impurity elements, at different exposures are measured and O. D. values are plotted against log exposure. Exposures, Es and Ei, at a particular O. D. on the linear portion of the plot, are substituted in the above equation to compute Ci more precisely. The data are further refined by taking into account the (i) relative sensitivities of singly charged ions (ii) relative areas of spectral lines and (iii) relative intensities of singly charged to multiply charged ions of the matrix and impurity elements. Ahearn[2] should be consulted for further details on the automatic evaluation of mass spectral data and computation of analytical results.

Whenever SSMS survey-analysis results indicate the presence of some elements at concentration $>$ 10 ppm and a precise analysis for one or more of those elements is needed, and feasible by AAS, then the sparked sample electrodes are dissolved in high purity acids and diluted to a solution containing 20 mg of matrix element per ml. A Varian AA-6 atomic absorption spectrometer is used for this analysis. Recommended optimum parameters are chosen for each element. Absence of chemical interference is ascertained by the standard addition technique. Scale expansion is employed wherever feasible. Molecular absorption/scattering is corrected for, using a hydrogen lamp.

RESULTS AND DISCUSSION

A research and development programme for the preparation and production of high purity materials calls for analytical support, at various stages. These include (i) determination of impurities in the raw material, which is generally of 99.0 - 99.9% purity, (ii) determination of specific impurities during the purification processes and (iii) compositional characterisation of high purity materials. Raw materials can be analysed conveniently by emission spectrography or by a combination of one or more of other analytical techniques. Among the several combinations of analytical techniques feasible for the analysis required at stages (ii) and (iii) listed above, one pragmatic approach seems to be the combination of SSMS and AAS. Materials that are generally analysed by SSMS are listed by Webster[8]. The precision of the results is often adequate for the end use.

AAS can be employed to determine several impurities at 10 ppm and above with a precision of five to ten percent. Some typical results obtained on the analysis of high purity materials are discussed below.

Table 2 gives the results on the analysis of (i) single crystal germanium prepared from poly-crystalline material and (ii) the head, middle and tail regions of zone- refined indium. Though the results are semi-quantitative in nature, they do indicate the pattern of segregation of impurities in a multi-pass zone-refined material. Results obtained on high purity gallium, lead and antimony are given in Table 3.

This combination approach has been applied for the analysis of nuclear-fuel-grade uranium. The aim was to correlate the performance of fuels fabricated from uranium metal from two batches of production to their compositional characteristics. Apart from the results reported in Table 4, the other elements of nuclear interest, such as B, Hf and the rare earths were analysed for and found to be below permissible limits. Hence, the differences in performance could not be attributed to the impurities. Another example of such an application was the certification of two samples of zinc, with respect to the impurity content. As the results given in Table 4 show, the samples were significantly different with respect to Cd and Pb content.

TABLE 2. Concentration of impurities in germanium and indium by SSMS.

Element	Germanium		Indium		
	Poly crystalline	Single crystal	Head	Middle	Tail
Aluminium	< 0.02	< 0.02	-	-	-
Copper	< 0.05	< 0.05	0.3	0.1	3.0
Zinc	< 0.1	< 0.1	-	-	-
Tin	0.2	0.2	0.2	< 0.2	2
Indium	0.07	< 0.07	-	-	-
Tellurium	-	-	0.6	< 0.2	2
Lead	-	-	0.6	< 0.2	2

All values are in μg/g

TABLE 3. Concentration of impurities in gallium, lead and antimony by SSMS.

Element	Gallium	Lead	Antimony
Aluminium	0.2		
Iron	0.1	0.1	0.5
Nickel	0.1	0.1	0.2
Copper	0.1	0.1	< 0.08
Zinc	< 0.3		
Germanium	< 0.5		
Cadmium		< 0.05	
Tin		0.1	< 0.2
Antimony		0.03	-
Bismuth		< 0.1	< 0.1

All values are in μg/g

TABLE 4. Concentration[a] of impurities in uranium and zinc

Element	Uranium		Zinc	
	Normal	Defective	Normal	Defective
Iron[b]	40	12	17	29
Chromium	4	2	2	2
Copper[b]	1.1	0.6	9	8
Cadmium	0.03	0.03	3[b]	425[b]
Indium	0.08	0.08	11	4
Lead	< 0.03	0.3	4100[b]	2200[b]
Bismuth	0.05	0.2	0.2	0.2

[a]value in μg/g

[b]results by AAS; uranium was separated prior to atomisation in the flame.

Spectral interference is rather rare in SSMS; but it is a serious disadvantage, wherever it occurs. In a few cases, the impurity element can be estimated using a line due to a less abundant isotope or that due to a multiply charged ion, but with poorer sensitivity. The problem could be more severe if the matrix has several isotopes; for example, Al, Si, Fe, Sb in cadmium selenide could not be estimated, even at ppm levels due to spectral interference from cadmium (Table 5). Similarly tellurium, present even at 200 ppm level showed spectral interference. The presence of mass line at 31.5 (m/e) due to $^{126}Te^{4+}$ confirmed the formation of multiply charged ions and showed that sulphur or phosphorus could not be estimated at sub-ppm levels. Similarly the mass line at 62.5 (m/e) due to $^{125}Te^{2+}$ indicates that copper cannot be estimated even at ppm levels unless the available resolution is of the order of 3×10^3 to 10^5.

TABLE 5. Spectral interference in the analysis of cadmium selenide[a]

Element	Analytical line	Interference from	Resolution $m/\Delta m$[b]
Aluminium	27	$^{108}Cd^{4+}$	4800
Silicon	28	$^{112}Cd^{4+}$	21500
	29	$^{116}Cd^{4+}$	96600
Phosphorus	31	$^{124}Te^{4+}$	16300
Sulphur	32	$^{128}Te^{4+}$	7440
Iron	56	$^{112}Cd^{2+}$	3390
	57	$^{114}Cd^{2+}$	3470
Nickel	58	$^{116}Cd^{2+}$	3390
Copper	63	$^{126}Te^{2+}$	2810
	65	$^{130}Te^{2+}$	2550
Antimony	121	$(^{108}Cd\ ^{13}C)^+$	32700
	123	$(^{111}Cd\ ^{12}C)^+$	6×10^5
		$(^{110}Cd\ ^{13}C)^+$	45500

[a] Tellurium is present as an impurity at 200 ppm

[b] required to resolve the interference.

CONCLUSION

A combination of SSMS and AAS has been successfully employed as complementary techniques. In this approach, SSMS was used as a scanning technique of high sensitivity and the flame AAS for improved precision at major-trace concentration levels.

Among the mass spectrometric methods, the isotope dilution (ID) technique is known to provide precise and accurate analysis even at extremely low concentrations. ID-SSMS is one of the techniques adopted to certify SRM high purity zinc[9], iron[10] and platinum[11]. ID-SSMS is modified, by mixing the solid sample with electromagnetically enriched isotopes, and adopted in the analysis of biological and geological samples[12, 13], coal ash[14] and fly ash[14].

Similarly, AAS can also be used for the determination of impurities at ppb levels, using preconcentration methods[15, 16]. The full realisation of the potential depends on the ingenuity of the analytical chemist in keeping the blank, from chemicals, apparatus and laboratory environment, at a few percent of the analyte concentration.

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