

B. A. R. C.-797

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GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

SETTING UP OF NUCLIDE GRAF-3S SPARK SOURCE
MASS SPECTROMETER FOR THE ANALYSIS OF HIGH
PURITY MATERIALS

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T. R. Mahalingam, P. Murugaiyan, K. S. Sonni
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BHABHA ATOMIC RESEARCH CENTRE
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URANIUM

SILICON

SAMPLE PREPARATION

SENSITIVITY

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1. INTRODUCTION

A spark source mass spectrometer is almost ideally suited to assess the purity of semi-conductors and nuclear grade and high purity materials (better than four nines). Dempster⁽¹⁾ was the first to demonstrate the potentialities of the spark source mass spectrometer as an analytical tool in 1935. Later in 1954, Hannay and Ahearn⁽²⁾ achieved a detection limit of the order of 0.1 ppm atomic. Now commercial equipments are available with detection limits of the order of 1-10 ppb atomic. The Analytical Chemistry Division purchased a Nuclide's GRAF-3S Spark source mass spectrometer in 1970 to improve the analytical capabilities of the Division. This report describes the setting up of the equipment and its use in the analysis of high purity materials.

2. SETTING UP THE SSMS FACILITY

Engineers from M/s. Nuclide Corporation, USA, had come to BARC to set up and demonstrate the performance of the equipment. After assembling the various components, the spectrometer was evacuated by rotary and diffusion pumps. The electrostatic and magnetic analyser regions were then isolated and allowed to be pumped down differentially, day and night, by 50 and 100 l/s ion pumps respectively. Even after several days of pumping, the pressure in the magnetic analyser was not better than 2×10^{-6} torr.

Meanwhile, the equipment was aligned for double-focussing conditions using thermal ionization source.

When attempts of leak hunting with a helium leak detector, having a detection limit of 10^{-9} std.cc/sec., were unsuccessful, the electrostatic and magnetic analysers (without the ion pumps) were baked for about 50 hours and at about 150°C . After cooling, a leak ($\sim 10^{-3}$ std.cc/sec.) was found near the SS weld region of the top pole of the magnet. On closing this, the vacuum improved, but to 2×10^{-7} torr only. Under these conditions the spectrometer was deemed to be capable of analysing impurities at 100 ppb level.

At 10^{-7} torr, there was considerable fogging of photographic plates. Appearance of spurious lines due to charge transfer collisions cannot be ruled out. Hence it was decided to improve the vacuum. We intensified our leak hunting using 'Veeco' helium leak detector, whose sensitivity was one order of magnitude better. The analyser and conditioning chamber regions were pumped with 350 l/s diffusion pump, its out-let being connected to the test port of the leak detector. Even then, no leak could be located. At this stage it became debatable whether there is a real leak (10^{-5} std.cc/sec.) in the system. So we started analysing a few silicon samples, which were not so pure.

When the pressure increased beyond 5×10^{-7} torr, the analyser regions including the ion pumps were repeatedly baked (for about 50 hours around 150°C) and cooled slowly. Pressure and temperature were continuously monitored during baking and cooling. In one such operation the pressure came down to 7×10^{-8} torr at 45°C , but on further cooling, it remained

steady for nearly 2 hours and then increased to 8×10^{-7} torr in about 3 hours. Suspecting leak(s), methanol was sprayed at several joints. When sprayed near the SS weld region of the top pole piece of the magnet, the pressure suddenly had fallen down to 2×10^{-8} torr. It increased again to 10^{-7} torr range after the evaporation of the solvent. The specific spot (which was found to be quite close to the earlier one) was located and closed. After this, the pressures were less than 1×10^{-8} torr and 2×10^{-8} torr in the electrostatic and magnetic analysers respectively. However, on continuous analysis of samples for about three months, the pressure slowly increased to 1×10^{-7} torr. Since then the spectrometer was baked periodically for about 30 hours at 120°C . Leaks did develop on more than one occasion at the top pole piece welds. Hence it was decided to modify the pumping system for the magnetic analyser region to eliminate leaking totally, lest the weld may become weak.

Utek Boettvac pump, which is a combination of ion pump (150 l/s) and titanium sublimation pump (1000 l/sec. speed for condensable vapours) was installed in place of the 100 l/s ion pump. Since then, it has become a matter of routine to pump down to 1×10^{-8} torr and less in the magnetic analyser from atmospheric pressure in about three hours.

3. ANALYSIS OF SAMPLES

The analytical procedure can be divided into two sections:

- (i) sample preparation, sparking and recording of exposures and
- (ii) evaluation of photographic plate and estimating the impurities. As these are discussed in detail in literature⁽³⁻⁵⁾ these are described briefly, followed by the analytical work carried out so far.

3.1 Sample Preparation, Sparking and Recording of Exposure

Conducting materials like Sn, Cd, In, Pt and Pt-Rh alloys, and semi-conductors like Si were machined to size (2 mm x 2 mm and 20 mm long), chemically etched and then used as electrodes. Thoria, silica and alumina were mixed with high purity graphite and then briquetted. Hydrofluoric acid was evaporated to a small volume, mixed with graphite and briquetted. Optimum pulse length, pulse rate and spark voltage were chosen, and maintained constant during all the exposures. 15 kV accelerating voltage and 11500 G magnetic field were employed to record the spectra. The electrodes were pre-sparked to remove surface impurities. As the ion-beam fluctuates very much during sparking a fraction of it is collected by the monitor before it enters the magnetic field. The line intensity on the photographic plate is related to the total charge collected by the monitor, expressed in coulombs (C).

13 exposures are recorded on a Q-2 plate in the range of $10^{-13}C$ to $10^{-7}C$, in steps of $\sqrt{10}$. With this wide range of exposure it is possible to detect several of the elements at 10 ppb and above. By recording the exposure of $10^{-6}C$, it is possible to detect elements at ten times lower concentration.

3.2 Evaluation of the Photographic Plate

The photographic plate is then developed following the manufacturer's instructions. Semi-quantitative and quantitative analysis can be carried out by visual and micro-photometric methods respectively. In the visual method the exposure E_1 necessary to produce a just detectable line for the most abundant isotope and E_2 that for the least abundant isotope of the matrix are read from the plate visually. The concentration

of the impurity C_1 can be calculated from the equation given below.

$$C_1 = \frac{E_B \cdot X}{E_1 \cdot 100} \cdot \frac{I_B}{I_1} \cdot 10^6 \text{ ppm atomic}$$

where x = percentage (atomic) of one of the elements in the matrix, I_B and I_1 are the natural abundances (%) of the isotopes on which the estimation is based. If there are more than one isotopes for the impurity element, then results are computed for both the isotopes and the average is taken.

In the micro-photometric method, the optical densities of the spectral lines are measured with micro-densitometer. The O.D. for the matrix and impurity isotope lines are plotted against log exposure. The exposures E_B and E_1 of the matrix and impurity isotopes at a specific O.D. say 0.20 are read from the graph and are substituted in the equation. Some more factors like line area, relative sensitivity coefficient etc., are to be included in the above equation for further refinement of the data.

Table 1 shows the types of samples analysed and their origin. Tables 2 to 4 show the results obtained for a few typical samples.

4. DISCUSSION

When the pressure in the magnetic analyser was 1×10^{-7} torr and when our attempts to locate a leak were unsuccessful, it became debatable, whether the leak is real or virtual. From a comparison of the rate of fall of pressure on cooling at different times (before and after achieving 1×10^{-8} torr) after baking and other observations, it became obvious that a treacherous leak remained undetected in the thick welds of the magnet pole piece, when the instrument was handed over to us.

Till recently there is no specific data available regarding the maximum pressure acceptable in the magnetic analyser for this type of mass

spectrometers. Recently M/s. Nuclide Corporation analysed zircaloy (NBS-SRM 1215) at 2.5×10^{-7} torr and 2×10^{-8} torr pressures in the analyser and reported⁽⁶⁾ higher background level, broadening of intense lines and charge exchange lines for Sn^{2+} to Sn^+ (in the m/e range of 230-250) at 2.5×10^{-7} torr. They did not find similar things at 2×10^{-8} torr. From this it is obvious that the pressure in the magnetic analyser should be improved to $1-2 \times 10^{-8}$ torr. It is also obvious from our experience that it can be achieved only by baking periodically. It is pertinent to note that leaks developed in and around the same spot on more than one occasion of baking. Since periodic baking, resulting in leaks often, will seriously minimise the life of the spectrometer, it was decided to eliminate baking totally by modifying the pumping system. With the installation of 1000 l/s Hoostivac pump in the analyser region, vacuum of the order of 1×10^{-8} torr is easily achieved without baking at all. With the improvement on the vacuum, the guaranteed detection limit was obtained. The downtime of the spectrometer was much less than 10% now.

Data in Table 2 gives the relative purities of imported silicon and the one prepared at Chemical Engineering Division, B.A.R.C. It shows that phosphorus is the main impurity in the silicon prepared in our Centre. The results also show that the silicon is getting contaminated with common impurities while removing the tantalum by dissolution and washing. The Table 3 shows the extent of concentration of impurities at the tail end on zone-refining of indium metal.

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6. Nuclide Product Bulletin No.1340-0573

Table 1

NATURE OF SAMPLES ANALYSED

Sr. No.	Type of Sample	Received from
1.	Si, SiO ₂	Chemical Engineering Division, BARC
2.	In,Sn,Sb,Cd,Bi,GaP	Chemistry Division, BARC and Nuclear Fuel Complex, Hyderabad
3.	Ag, Au, and Pt	Technical Physics Division, BARC and Instrumentation India Ltd., Kota
4.	Cr	Central Electrochemical Research Institute, Karaikudi
5.	ThO ₂	Indian Rare Earths Ltd., Bombay
6.	HF	M/s. Navin Fluorine Industries, Bombay

Table 2

ANALYSIS OF SILICON

Sr. No.	Element	Silicon deposited on		Doped silicon (imported) ppm
		Tantalum ppm	Silicon ppm	
1.	Magnesium	10	0.5	1
2.	Calcium	10	0.1	2
3.	Copper	10	< 0.05	< 0.05
4.	Boron	< 0.01	0.01	< 0.01
5.	Phosphorus	0.1-2	0.1-2	0.03
6.	Arsenic	< 0.05	< 0.05	< 0.05
7.	Antimony	< 0.1	< 0.1	200 (Dopant)
8.	Tantalum	< 0.1	< 0.1	< 0.1

Table 3

ANALYSIS OF ZONE-REFINED INDIUM

Sr. No.	Element	Head ppm	Middle ppm	Tail ppm
1.	Magnesium	1	4	4
2.	Calcium	2	6	12
3.	Nickel	0.1	< 0.05	0.3
4.	Copper	0.3	0.1	3.0
5.	Cadmium	2	< 0.2	0.6
6.	Tin	0.2	< 0.2	2
7.	Tellurium	0.6	< 0.2	2
8.	Lead	0.6	< 0.2	2

Table 4

ANALYSIS OF URANIUM METAL

Sr. No.	Element	Sample	
		A ppm	B ppm
1.	Silicon	30	10
2.	Chromium	4 (3.7)	1 (<u>/2</u>)
3.	Manganese	4 (2.1)	4 (3.4)
4.	Nickel	5 (5.8)	2 (2)
5.	Iron	40	12
6.	Copper	2 (1.1)	0.6 (0.6)
7.	Arsenic	0.2	0.06
8.	Molybdenum	0.3	0.03
9.	Zirconium	0.4	1.0
10.	Lead	< 0.03	0.3
11.	Bismuth	0.05	0.2

Values given in the brackets are obtained by atomic absorption spectrometry

