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SOLID SAMPLE MASS SPECTROMETER ANALYSES OF ENRICHED STABLE ISOTOPES

J. R. Walton

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STABLE ISOTOPES DIVISION

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Joe R. Walton

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SOLID SAMPLE MASS SPECTROMETER ANALYSES OF ENRICHED STABLE ISOTOPES

Joe R. Walton

ABSTRACT

Solid Sample mass spectrometer analyses have been made on the enriched stable isotopes of 53 elements. The elements analyzed, the compounds used, the oven materials employed, the ions monitored, and some special techniques of analyses are reviewed.

SOLID SAMPLE MASS SPECTROMETER ANALYSES OF ENRICHED STABLE ISOTOPES

Joe R. Walton

This paper describes some of the methods and techniques employed in the mass spectrometric analysis of isotopically enriched materials. The work was performed as an integral part of the production and preparation of electromagnetically enriched stable isotopes. The Stable Isotopes Division of the Oak Ridge National Laboratory in Oak Ridge, Tennessee, has processed 53 elements, representing more than 217 isotopes.

Attemps were always made to analyze the material in the same chemical form in which the material is furnished. In most instances the sample was in the form of an oxide. Indeed, other compounds could have been studied with greater ease, but this would mean that intervening chemistry would be necessary with possible contamination by natural material of precious enriched isotopes. In addition, since only small quantities of the materials were available for assay the amounts needed for conversion could be prohibitive. The elemental ions were monitored when possible to eliminate the necessity of correction for isotopes of other elements that may be present in the complex ion.

Table 1 is a list of elements analyzed, the chemical compounds used, the oven material employed, and the ions monitored.

No reference is made to the isotopic purity of the enriched isotopes since this information may be found in the Stable Isotope Inventory and Price List[1].

An all metal, six-inch radius, 60° sector type mass spectrometer was used for these analyses (Figure 1). The main difficulty in the analyses of a low vapor pressure solid is devising an efficient method for vaporizing and ionizing the

[1]The Stable Isotope Inventory and Price List is available by addressing correspondence to: Stable Isotopes Division, Oak Ridge National Laboratory, Post Office Box Y, Oak Ridge, Tennessee.

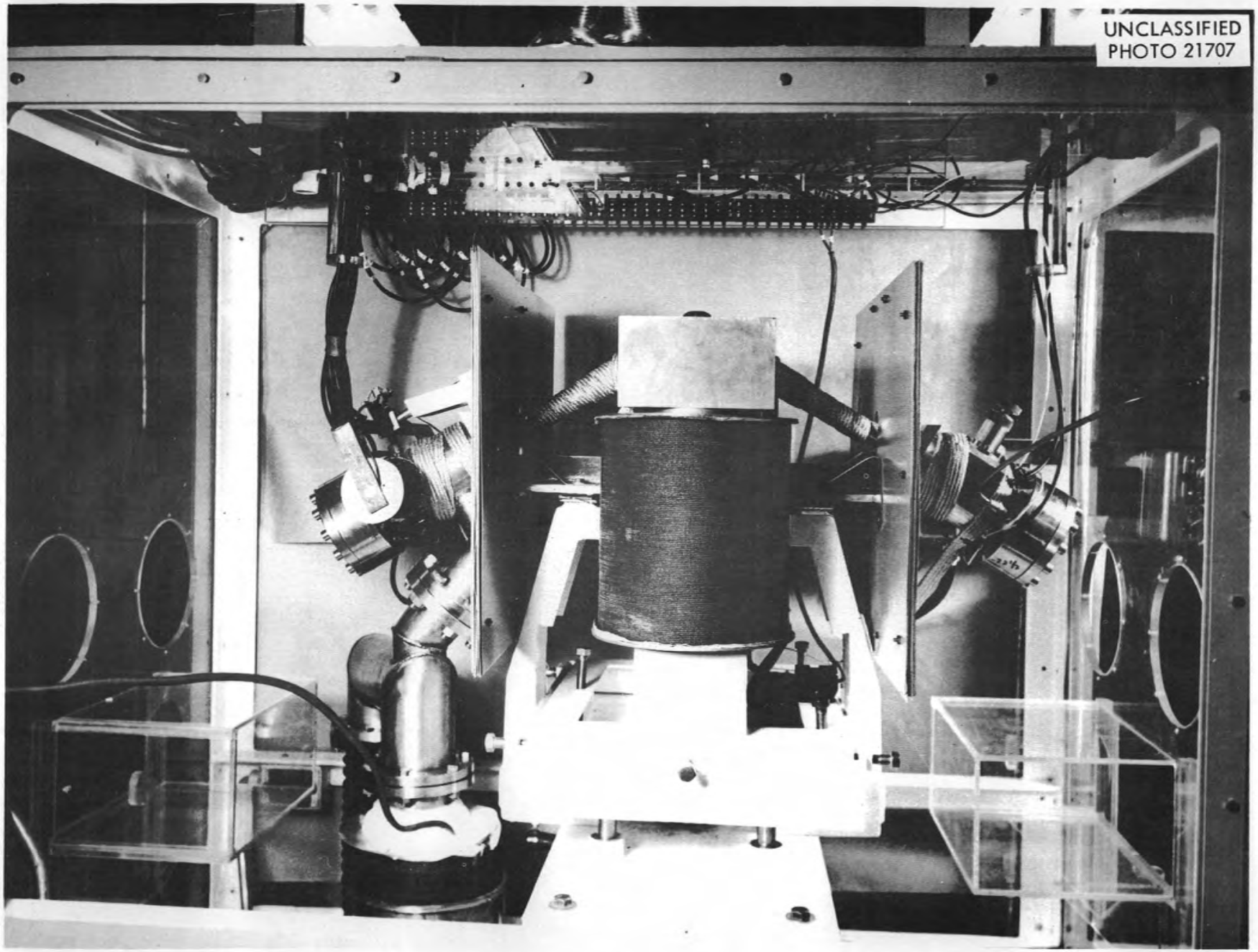

Fig. 1. All Metal 60° Mass Spectrometer.

Table 1

SOURCE AND CHEMICAL COMPOUNDS USED IN THE ANALYSIS OF ENRICHED STABLE ISOTOPES

Atomic Number	Element	Sample Material	Oven Material	Source Type: Surface Ionization	Source Type: Electron Bombardment	Ions Measured
3	Lithium	LiI, Li_2SO_4	Ta		X	LiI^+
5	Boron	B, B_4C	Ta		X	B^+
6	Carbon	C	Ta		X	C^+
12	Magnesium	MgO	Ta	X		Mg^+
14	Silicon	SiO_2	Ir	X		SiO^+
16	Sulfur	As_2S_3	Ta		X	AsS^+
17	Chlorine	NaCl, AgCl	Ta		X	Cl^+
19	Potassium	KCl	Ta	X		K^+
20	Calcium	CaI_2	Ta		X	CaI^+
22	Titanium	TiO_2	Ta	X		TiO^+
23	Vanadium	V_2O_5	Ta		X	V^+
24	Chromium	Cr_2O_3	Ta	X		Cr^+
26	Iron	Fe_2O_3	Ta		X	Fe^+
28	Nickel	$NiO, NiSO_4$	Ta		X	Ni^+
29	Copper	$CuO, CuBr_2$	Ta		X	Cu^+

Table 1 cont.

Atomic Number	Element	Sample Material	Oven Material	Source Type: Surface Ionization	Source Type: Electron Bombardment	Ions Measured
30	Zinc	Zn,ZnO	Ta		X	Zn^+
31	Gallium	Ga_2O_3	Ta	X		Ga^+
32	Germanium	GeO_2	Ta		X	Ge^+
34	Selenium	Se_8	Ta		X	Se^+
35	Bromine	KBr	Ta		X	Br^+
37	Rubidium	RbCl	Ta	X		Rb^+
38	Strontium	$SrCO_3$,$Sr(NO_3)_2$	Ta	X		Sr^+
40	Zirconium	ZrO_2	Ta	X		ZrO^+
42	Molybdenum	MoO_3	Ta		X	MO^+
44	Ruthenium	Ru	Ir	X		Ru^+
46	Palladium	Pd	Ta		X	Pd^+
47	Silver	AgCl,AgI,AgBr	Ta		X	Ag^+
48	Cadmium	CdS	Ta		X	Cd^+
49	Indium	In_2O_3	Ta	X		In^+
50	Tin	SnO_2	Ta		X	Sn^+
51	Antimony	Sb	Ta		X	Sb^+
52	Tellurium	Te,TeO	Ta		X	Te^+
56	Barium	$BaCO_3$	Ta	X		Ba^+

Table 1 Cont.

Atomic Number	Element	Sample Material	Oven Material	Source Type: Surface Ionization	Source Type: Electron Bombardment	Ions Measured
57	Lanthanum	La_2O_3	Ta	X		LaO^+
58	Cerium	CeO_2	Ta	X		Ce^+
60	Neodymium	Nd_2O_3	Ta	X		NdO^+
62	Samarium	Sm_2O_3	Ta	X		Sm^+
63	Europium	Eu_2O_3	Ta	X		Eu^+
64	Gadolinium	Gd_2O_3	Ta	X		GdO^+
66	Dysprosium	Dy_2O_3	Ta	X		Dy^+
72	Hafnium	HfO_2	Ta	X		HfO^+
73	Tantalum	Ta_2O_5	Ir		X	TaO_2^+
74	Tungsten	WO_3	Ta		X	W^+
75	Rhenium	Re_2O_7	Ta		X	Re^+
77	Iridium	Ir	Ta		X	Ir^+
78	Platinum	Pt	Ta		X	Pt^+
80	Mercury	$Hg(NO_3)_2$	Ta		X	Hg^+
81	Thallium	Tl_2O_3	Ta	X		TlO^+
82	Lead	Pb,PbO	Ta		X	Pb^+

material under study. The Nier type source[2] was modified by replacing the ion chamber assembly by a stainless steel block in which was milled an ion chamber area. An assembly was constructed so that the oven could be fastened in place and removed without disturbing the remainder of the source.

Figure 2 shows a cylindrical resistance heated oven. These ovens are constructed from both tantalum and platinum thus making it possible to heat samples to temperatures that approach the melting point of these metals (tantalum 2850° C platinum 1755° C). Iridium strips instead of cylinders have also been used; iridium being brittle cannot be formed as readily as tantalum or platinum. The ovens are small and contain no thermal insulating materials so that the outgassing period is reduced. These cylindrical ovens are easily fabricated by drawing sheet stock 60 mils wide, and 1 or 2 mils thick through a wire draw plate until a long cylindrical tube is formed. The cylinder is not completely closed. The open tubes are cut into one-half inch lengths and twenty mil wire (tantalum or platinum) is inserted into the ends and spot welded in place. These small ovens are then spot welded to the tantalum legs of the oven subassembly which locates the oven in the region of the ionizing electron beam. A well regulated A.C. power supply furnishes the power to the oven.

The procedure for loading an oven is simple. A small amount usually about 25 to 50 μg of dry solid material is placed in the oven. If the material can be put in solution, it may be painted on the oven. Double distilled water, distilled "center cut" nitric acid, and acetone have been used as solutes. Some materials will not go in to solution readily, in which case it may be necessary to use a binding material to bind the sample to the oven. Sauereisen[3] cement and borax have been used as binders. However, one must be careful that there are no interfering masses produced from the binders. When using the iridium strip

2 Nier, A. O. Rev. Sci. Insts., 1940, 11, 212.
3 Hand, John E. Rev. Sci. Instr. 24, 181 (1953).

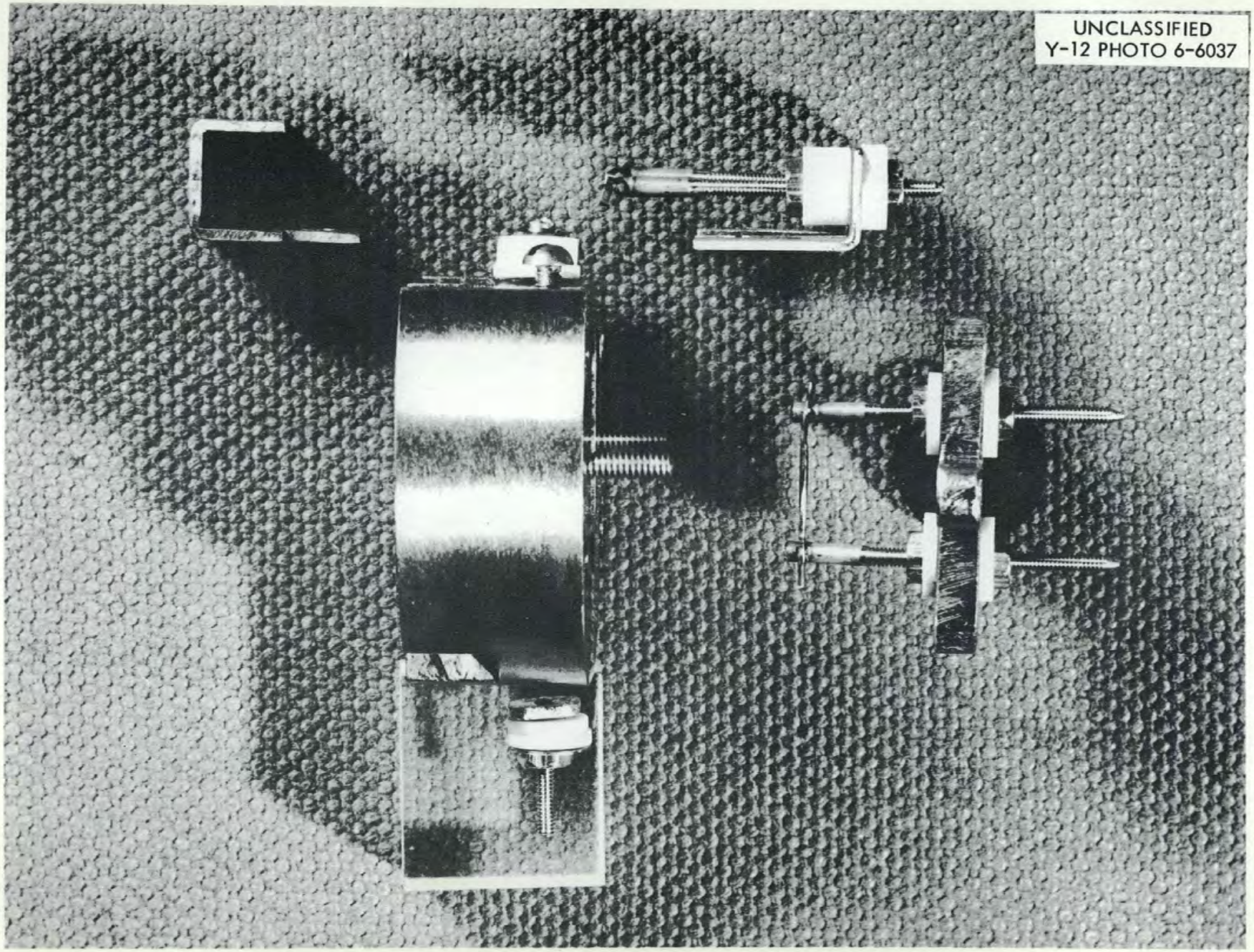

Fig. 2. High Temperature Mass Spectrometer Oven.

oven, the material is fused to the strip by passing current through the iridium. This operation may be carried out in open air or under an inert atmosphere since iridium does not oxidize readily when heated in open air.

Ions produced with this type of source may be formed either by direct thermal emission from the oven or by the electron bombardment of neutral particles. In the case of ionization by electron bombardment, residual gases or oil vapors present in the source region are also ionized. This may produce an objectionable background unless there is sufficient waiting period. The materials present in and on the oven must be outgassed; and this also contribures to the background.

There are a number of other advantages of the thermal ionization method.

1. The emitting surface can be small.

2. The amount of material needed for analysis can be small; 5 to 50 μg range.

3. Ions formed from other origins than the sample materials are practically non-existent as they may be formed only by secondary or tertiary processes. Memory and background problems are no longer considered troublesome.

Atoms and molecules are evaporated from a hot surface and have a probability of being evaporated as positive ions, according to the following equation[4]:

$$\frac{n+}{n^{o}} = \exp \frac{e(W - \phi)}{KT}$$

$\frac{n^{+}}{n^{o}}$ = ratio of charged to uncharged particles of same species

e = electronic charge

W = work function of the oven surface

ϕ = ionization potential of the species being studied

K = Boltzman's constant

T = temperature in °K

[4]Langmuir, I. and Kingdon, K. H. Proc. Roy. Soc. A 107, 61 (1925)

This equation is only a rough guide in practice as the work function of the oven is very dependent on surface conditions and the contact between the oven and the sample material varies greatly. It is best to have a small strip of metal with a high work function.

As has been pointed out, the advantages of thermal ionization are great but, there are some disadvantages such as preferential evaporation. Usually, as in the case of light elements such as lithium, it is better to move to a higher mass range (lithium iodide mass 133 and 134)to overcome the fractionation. There is an added advantage at this mass range because the discrimination of the spectrometer itself is also reduced.

Greater thermal ion efficiency and higher ion intensities have been experienced while using Sauereisen and borax binders. This may be due to better thermal contact between oven and sample materials, or a chemical action between the components of the binders and oven material may cause an increase in the effective work function of the oven surface. Very little trouble has been experienced with these binders except the outgassing time is slightly increased, and at times small bursts of gas have been noticed.

Multiple sample techniques have facilitated analyzing a greater number of samples in less time. The down time between analyses has been practically eliminated by placing as many as four samples on a single oven and analyzing them in the descending order of their vapor pressures. The materials must be selected so there is no mass over-lap and there should be a wide difference in vapor pressures. The oven is placed in the spectrometer and the first analysis is made; one moves then to the mass region where the next highest vapor pressure material is to be expected and so on until all the materials have been examined.

CONCLUSION

Sufficient information and methods are now available for carrying out an isotope analysis on any of the elements that have stable nuclides.

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