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**MASS SPECTROMETRIC MEASUREMENTS
OF NATURAL ISOTOPIC SPECTRA**

By

R. F. HIBBS

Y-12 PLANT

CARBIDE AND CARBON CHEMICALS CORPORATION

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CHEMICAL DIVISION

Mr. J. M. Herndon, Superintendent

ASSAY LABORATORY DEPARTMENT

Mr. R. F. Hibbs, Superintendent

MASS SPECTROMETRIC MEASUREMENTS OF NATURAL ISOTOPIC SPECTRA

ABSTRACT

The natural isotopic composition of eighteen stable elements has been determined with the mass spectrometer. The methods used meet the requirement of small sample consumption and are suitable for the analysis of enriched materials. Brief descriptions of the chemical preparation of compounds, the sample handling techniques and the ions measured are included.

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1

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ASSAY LABORATORY DEPARTMENTMASS SPECTROMETRIC MEASUREMENTS OF NATURAL ISOTOPIC SPECTRAINTRODUCTION

In connection with the electromagnetic separation of stable isotopes at the Y-12 Plant of Carbide and Carbon Chemicals Corporation, the Assay Laboratory Department is confronted with the development of suitable methods of isotopic analysis of the enriched materials. A major consideration in these analyses is the desirability of small sample consumption coupled with the attainment of high accuracy. This requirement necessitates the preparation of chemical compounds from a small amount of starting material, yielding a product that is reproducible in chemical and physical behavior. Consequently, the methods devised are oftentimes a compromise between the most suitable physical technique and the most expedient chemical preparation. In all cases, these methods are tested using natural material. This permits the necessary physical and chemical development, provides evaluation of the results and yields information, concerning the natural isotopic composition of the element in question. Many of the methods presented in this paper have been used for the isotopic analysis not only of the separated samples, but also of these materials following their use in tracer work.

EXPERIMENTAL

The instrument used for these measurements was the Nier type, 60° mass spectrometer. Ionization was accomplished by slow electron bombardment of the sample vapors or thermal emission of the ions from heated solids. The ions thus obtained were accelerated by a potential of 2000 volts. Scanning was accomplished by varying the current through the electromagnet, taking precaution not to change the accelerating voltage. Following separation of the ions by the conventional sector magnet, the currents obtained were measured by an FP-54 electrometer tube. The voltage developed across the grid resistor of the tube was balanced by a voltage from a precision potentiometer, using a galvanometer as a null indicating device. In some cases, the ion currents were measured by a VX-41 electrometer tube, driving a standard Brown Elektronik recording potentiometer. The operating vacuum, which was achieved by a three-stage, self-fractionating, oil diffusion pump, was of the order of 5×10^{-7} mm of mercury. A liquid nitrogen trap was provided to prevent contamination of the spectrometer tube by the oil vapor. The resolution between mass units in all cases was perfect.

Considerable care was taken to eliminate mass interference since this was the largest potential source of error. Chemical purity of the compound used was of primary importance. Reaction products, other than the compound desired, unreacted reagents and water were some of the impurities to be

avoided. The use of compounds affording multiple ions was helpful in that the ratios could be measured at several mass positions. Another approach was to use an entirely different compound, but unfortunately this was not always possible. Each determination was the result of at least ten ratio measurements and the variation of the ratios with time was used as an indication of possible mass interference. In all cases, the above precautions were taken, and the mass region adjacent to the measured ions was free of impurities.

The sample handling technique for these analyses depended upon the type of compound used. Those materials which were gaseous at room temperature were admitted into the instrument through a controllable leak. Materials with sufficient vapor pressure at temperatures between 25°C and 300°C were distilled through a heated delivery tube. For temperatures in excess of 300°C, small electrically heated furnaces were constructed, and the sample material placed in Pyrex, quartz or platinum retorts. These furnace-retort combinations were oriented directly above the ionizing case of the source and were provided with thermocouples for temperature measurements. Another type of furnace used for these higher temperatures consisted of a spiral of .010" tungsten wire, supported directly over the electron beam within the ionizing case. Sample materials were coated on the spiral, which was heated by electrical conduction, and the vapors sublimed into the electron beam.

ERRORS

The errors quoted are expressed in terms of the standard deviation of an individual determination and represent only the precision of the measurement. No estimate of possible bias was made, though in all cases, the instrument was so adjusted, and operating conditions were such that known sources of systematic error would be minimized. It is evident from examination of the data that the type of chemical compound used exerted the largest influence on the variation between this and other published data. In all cases, variations between ion sources and instruments were less than those obtained between chemical compounds.

RESULTS

Oxygen

This element was analyzed by admitting the tank gas into a mass spectrometer through a capillary leak. Measurements were made on the O_2^+ ion at masses 32, 33 and 34. In addition, determinations were made upon oxygen electrolyzed from tap water, and again the O_2^+ ion was measured. The results of twelve determinations with one instrument are shown below:

Mass	16	17	18
Tank Gas	99.770 ± 0.05	0.035 ± 0.009	0.195 ± 0.01
Water	99.775 ± 0.06	0.035 ± 0.008	0.190 ± 0.01
Thode & Smith ⁽¹⁾ : Electron ionization of O ₂ from water, atmosphere, tank O ₂ , Fe ₃ O ₄ & PbO ₂ .	99.757	0.039	0.204

Neon

Purified neon gas was admitted to a mass spectrometer through a capillary leak. Measurements were made on the Ne⁺ ion at masses 20, 21 and 22. The results of seven determinations with one instrument are shown below:

Mass	20	21	22
This Work	89.99 ± 0.03	0.30 ± 0.01	9.72 ± 0.01
Dibeler, Mohler & Reese ⁽²⁾ : Electron ionization of purified neon gas.	90.51	0.28	9.21

Silicon

Silicon tetrafluoride, prepared by fluorination of the dioxide with CoF₃, was admitted into the mass spectrometer through a capillary leak and measurements were made on the SiF₃⁺ ion. The results of eighteen determinations with three instruments are shown below:

Mass	28	29	30
This Measurement	92.19 ± 0.06	4.70 ± 0.03	3.12 ± 0.04
Inghram ⁽³⁾ : Electron ionization of SiF ₄ gas.	92.28	4.67	3.05
White & Cameron ⁽⁴⁾ : Electron ionization of SiF ₄ gas.	92.16	4.71	3.13
Williams & Yuster ⁽⁵⁾ : Electron ionization of SiF ₄ gas.	92.27	4.68	3.05
Ney & McQueen ⁽⁶⁾ : Electron ionization of SiF ₄ gas.	92.24	4.69	3.07

Chromium

A sample of chromium trichloride was prepared by reacting the sesqui-oxide with carbon monoxide and chlorine. The CrCl_3 was distilled into the electron beam from a platinum retort at approximately 365°C , and measurements were made on the metallic ion. These results were obtained from fifteen determinations made with one instrument.

Mass	50	52	53	54
This Measurement	± 4.41 ± 0.06	± 83.46 ± 0.11	± 9.54 ± 0.06	± 2.61 ± 0.09
White & Cameron ⁽⁴⁾ : Electron ionization of CrCl_3 .	4.31	83.76	9.55	2.38
Nier ⁽⁷⁾ : Electron ionization of chromium metal vapor.	4.49	83.78	9.43	2.30

Iron

For natural abundance measurements of this element, anhydrous ferric chloride, prepared by the reaction of chlorine on the metal, was used. This material was distilled into the mass spectrometer through a heated delivery tube at a temperature of 285°C . Measurements on the Fe^+ ion, resulting from seventeen determinations with two instruments are shown below:

Mass	54	56	57	58
This Measurement	± 5.903 ± 0.015	± 91.52 ± 0.02	± 2.245 ± 0.011	± 0.335 ± 0.003
White & Cameron ⁽⁴⁾ : Electron ionization of FeCl_2 .	5.81	91.64	2.21	0.34
Valley & Anderson ⁽⁸⁾ : Electron ionization of Fe metal vapor.	5.83	91.7	2.16	0.31
Nier ⁽⁷⁾ : Electron ionization of Fe metal vapor.	6.0	91.6	2.1	0.28

Zinc

Zinc metal was distilled into the instrument through a heated delivery tube at a temperature of 150°C . Measurements were made on the Zn^+ ion. Fifteen

determinations were made with two instruments.

Mass	64	66	67	68	70
This Measurement	48.87 ± 0.10	27.62 ± 0.10	4.12 ± 0.09	18.71 ± 0.10	0.69 ± 0.02
Leland & Nier ⁽⁹⁾ : Electron ionization of zinc iodide.	48.89	27.81	4.07	18.61	0.620
Aston ⁽¹⁰⁾ : Photometry.	50.0	27.3	3.9	17.4	0.5

Gallium

Gallium iodide was prepared by reacting metallic gallium with an excess of iodine in an atmosphere of helium at 300°C. At the completion of the reaction, the excess iodine was sublimed off, yielding pure GaI₃. This sample was admitted to the mass spectrometer by distilling through a heated delivery tube at approximately 60°C. Measurements on the GaI₂⁺ ion which are the result of forty-five determinations with four instruments are shown below:

Mass	69	71
This Measurement	60.00 ± 0.07	40.00 ± 0.05
Inghram ⁽¹¹⁾ : Electron ionization of gallium oxide vapor.	60.2	39.8
Sampson & Bleakney ⁽¹²⁾ : Electron ionization of gallium sesqui-oxide vapor.	61.5	38.5

Selenium

Selenium metal was fluorinated with CoF₃ in a monel reactor. The resulting SeF₆ was admitted into the spectrometer through a capillary leak, and the gas ionized by slow electron bombardment. Twelve determinations were made with one instrument on the SeF₅⁺ ion.

Mass	74	76	77	78	80	82
This Measurement	0.96 ± 0.03	9.12 ± 0.03	7.50 ± 0.14	23.61 ± 0.05	49.96 ± 0.21	8.84 ± 0.08
White & Cameron ⁽⁴⁾ : Electron ionization of Se metal and SeF ₆ .	0.87	9.02	7.58	23.52	49.82	9.19

Bromine

For natural abundance measurements on this element, a sample of commercially prepared, reagent grade silver bromide was used. This material was distilled from a pyrex retort at a temperature of 300°C, and the Br^+ ion was measured. The results of eleven determinations with one instrument are shown below:

Mass	79	81
This Measurement	50.57 ± 0.07	49.43 ± 0.06
White & Cameron ⁽⁴⁾ ; Electron ionization of silver bromine.	50.51	49.49
Williams & Yuster ⁽⁵⁾ ; Electron ionization of cobaltous bromide.	50.52	49.48
Blewett ⁽¹³⁾ ; Electron ionization of liquid bromine vapor.	50.6	49.4

Molybdenum

A sample of molybdenum oxytrichloride was prepared by reacting the oxide with carbon monoxide and chlorine. This material was admitted into the instrument through a delivery tube at room temperature. Abundances, measured on the metallic ion, resulting from twelve determinations with two instruments are shown below:

Mass	92	94	95	96	97	98	100
This Measurement	15.05 ± 0.01	9.35 ± 0.01	15.78 ± 0.04	16.56 ± 0.04	9.60 ± 0.01	24.00 ± 0.03	9.68 ± 0.01
Williams & Yuster ⁽⁵⁾ ; Electron ionization of Mo hexacarbonyl.	15.86	9.12	15.7	16.5	9.45	23.75	9.62
White & Cameron ⁽¹⁴⁾ ; Electron ionization of Mo pentachloride.	16.19	9.59	15.47	16.47	9.33	23.57	9.35
Valley ⁽¹⁵⁾ ; Electron ionization of Mo vapor.	14.9	9.40	16.1	16.6	9.65	24.1	9.25

Cadmium

Cadmium oxide was dissolved in hydrogen iodide and evaporated to dryness. The resulting cadmium iodide was distilled from a pyrex retort at 185°C, and the vapor was ionized by slow electrons. Measurements were made on the CdI^+ ion, and they are the result of nine determinations with one instrument.

Mass	106	108	110	111	112	113	114	116
This Measurement	1.22 ± 0.01	0.89 ± 0.02	12.43 ± 0.04	12.86 ± 0.04	23.79 ± 0.06	12.34 ± 0.05	28.81 ± 0.07	7.66 ± 0.03
White & Cameron(4): Electron ionization of CdCl_2 .	1.22	0.98	12.35	12.78	24.00	12.30	28.75	7.63
Leland & Nier(9): Electron ionization of CdI_2 .	1.215	0.875	12.39	12.75	24.07	12.26	28.86	7.58
Aston(10): Photometry.	1.5	1.0	15.6	15.2	22.0	14.7	24.0	6.0

Indium

Indium sesqui-oxide was dissolved in hydrochloric acid to form the trichloride. The InCl_3 was distilled from a platinum retort into the ionization region of a platinum iridium ion source at approximately 100°C. Measurements were made on the In^+ ion at masses 113 and 115. The results include fourteen determinations with two instruments.

Mass	113	115
This Measurement	4.16 ± 0.01	95.84 ± 0.01
White & Cameron(4): Electron ionization of InCl_3 .	4.23	95.77
Aston(10): Photometry.	4.5	95.5

Tin

Stannic chloride was prepared by the reaction of chlorine with the metal. The sample was admitted into the mass spectrometer through a capillary leak, and measurements were made on the Sn^+ ion. The results are comprised of twelve determinations with one instrument.

Mass	112	114	115	116	117	118	119	120	122	124
This Measurement	1.01 ± 0.03	0.68 ± 0.01	0.35 ± 0.03	14.28 ± 0.01	7.67 ± 0.05	23.84 ± 0.08	8.68 ± 0.01	32.75 ± 0.03	4.74 ± 0.04	6.01 ± 0.09
White & Cameron(4): Electron ionization of SnCl_2 .	0.90	0.61	0.35	14.07	7.54	23.98	8.62	33.03	4.78	6.11
Aston(10): Photometry.	1.1	0.8	0.4	15.5	9.1	22.5	9.8	28.5	5.5	6.8

Tellurium

Tellurium hexafluoride, prepared by fluorination of the metal with CoF_3 , was admitted to the spectrometer for the determination of natural tellurium. Since TeF_5^+ was most abundant, measurements were made on this ion. For these results, twenty-three determinations were made with three instruments.

Mass	120	122	123	124	125	126	128	130
This Measurement	0.090 ± 0.01	2.47 ± 0.01	0.89 ± 0.01	4.74 ± 0.02	7.03 ± 0.03	18.72 ± 0.05	31.75 ± 0.06	34.27 ± 0.05
White & Cameron(4): Electron ionization of TeF_6 .	0.091	2.49	0.89	4.63	7.01	18.72	31.72	34.46
White & Cameron(4): Electron ionization of Te metal vapor.	0.092	2.32	0.88	4.51	6.99	18.53	32.57	34.11
William & Yuster(5): Electron ionization of TeF_6 .	0.090	2.43	0.85	4.59	6.97	18.70	31.85	34.5

Cerium

Ceric oxide, prepared by heating ceric sulfate in air at 900°C, was coated on a heated tungsten spiral, and an intense beam of thermal ions was formed. The CeO^+ ion was the most abundant, and the results of fourteen determinations with one instrument are shown below:

Mass	136	138	140	142
This Measurement	0.195 ± 0.005	0.265 ± 0.003	88.449 ± 0.020	11.098 ± 0.033
Inghram(16): Thermal ionization from ceric oxide.	0.193	0.250	88.48	11.07

Hafnium

Hafnium oxide was reacted with carbon monoxide and chlorine to form hafnium tetrachloride. This material was admitted into the spectrometer through a heated delivery tube at 150°C. Measurements were made on the Hf^+ ion. The results include twelve determinations with two instruments.

Mass	174	176	177	178	179	180
This Measurement	0.18 ± 0.01	5.15 ± 0.02	18.39 ± 0.01	27.08 ± 0.04	13.78 ± 0.02	35.44 ± 0.06
Mattauch & Lichtblau(17):	0.18	5.30	18.47	27.10	13.84	35.11

Tungsten

For natural abundance measurements of tungsten, a sample of WOCl_4 was prepared by chlorination of tungsten oxide with hexachloropropene. This material was introduced into the spectrometer by use of a heated delivery tube. The temperature necessary for distillation was of the order of 60°C to 100°C, and the W^+ ion was the most abundant. Measurements on this ion are the result of sixteen determinations with three instruments.

Mass	180	182	183	184	186
This Measurement	0.143 ± 0.002	26.09 ± 0.01	14.24 ± 0.02	30.68 ± 0.01	28.85 ± 0.01
White & Cameron ⁽⁴⁾ : Electron ionization of tungsten hexafluoride.	0.126	26.31	14.28	30.64	28.64
Williams & Yuster ⁽⁵⁾ : Electron ionization of tungsten hexacarbonyl.	0.135	26.41	14.40	30.64	28.41
Inghram ⁽³⁾ : Electron ionization of tungsten hexafluoride.	0.122	25.77	14.24	30.68	29.17

Mercury

This element was analyzed by admitting the metal into a mass spectrometer through a heated delivery tube. Some application of heat to the delivery tube was necessary to adequately control the gas flow. The results of twenty-nine determinations with three instruments, using the Hg^+ ion, are shown below:

Mass	196	198	199	200	201	202	204
This Measurement	0.16 ± 0.03	10.02 ± 0.06	16.92 ± 0.07	23.10 ± 0.08	13.22 ± 0.06	29.72 ± 0.09	6.84 ± 0.06
Nier ⁽¹⁸⁾ : Electron ionization of Hg metal vapor.	0.15	10.11	17.03	23.26	13.17	29.56	6.72

Thallium

Thallium iodide, prepared by dissolving thallic oxide in hydriodic acid and evaporating to dryness, was used for the measurements of this element. The material was distilled into the mass spectrometer from a pyrex retort at 170°C, and measurements were made on the Tl^+ ion. These results are comprised of ten determinations with one instrument.

Mass	203	205
This Measurement	29.52 ± 0.05	70.48 ± 0.07
White & Cameron ⁽⁴⁾ : Electron ionization of Tl metal vapor.	29.46	70.54
Nier ⁽¹⁹⁾ : Electron ionization of Tl metal vapor.	29.1	70.9
Aston ⁽¹⁰⁾ : Photometry	29.43	70.57

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R. F. Hibbs

RFH:LJB

APPROVED:

J. M. Herndon

BIBLIOGRAPHY:

- (1) Thode & Smith: National Research Council of Canada, Atomic Energy Project, Report MC-57 (May, 1945).
- (2) Dibeler, Mohler & Reese: J. Research National Bureau of Standards 38, 617 (1947).
- (3) Inghram: Phys. Rev. 70, 653 (1946).
- (4) White & Cameron: Phys. Rev. 74, 991 (1948).
- (5) Williams & Yuster: Phys. Rev. 69, 556 (1946).
- (6) Ney & McQueen: Phys. Rev. 69, 41 (1946).
- (7) Nier: Phys. Rev. 55, 1143 (1939).
- (8) Valley & Anderson: Phys. Rev. 59, 113 (1941).
- (9) Leland & Nier: Phys. Rev. 73, 1206 (1948).
- (10) Aston: Mass Spectra and Isotopes (E. Arnold and Co., London, 1942).
- (11) Inghram, Hess, Brown & Goldberg: Phys. Rev. 74, 343 (1948).
- (12) Sampson & Bleakney: Phys. Rev. 50, 456 (1935).
- (13) Blewett: Phys. Rev. 49, 900 (1935).
- (14) White & Cameron: The Natural Abundance of Isotopes of Stable Elements, T.E.C. B-6.281.1.
- (15) Valley: Phys. Rev. 57, 1058 (1940).
- (16) Inghram, Hayden & Hess: Phys. Rev. 72, 967 (1947).
- (17) Mattauch & Lichtblau: Zeits. f. Physik, 111, 514 (1939).
- (18) Nier: Phys. Rev. 52, 933 (1937).
- (19) Nier: Phys. Rev. 54, 275 (1938).