31. *The Absolute Isotopic Abundance Ratio and the Atomic Weight of Natural Silver.*

By E. A. C. Crouch and A. H. Turnbull.

An examination of the isotopic abundance ratio in natural silver by means of the mass spectrometer has resulted in a value of 1·0733 ± 0·0043 for the absolute isotopic abundance ratio $^{107}Ag/^{109}Ag$. Specimens of commercial silver of diverse ages possess abundance ratios within the limits of the determinations and thus the calculated atomic weights are: chemical scale (O = 16) 107·8740 ± 0·0033; physical scale (^{16}O = 16) 107·9037 ± 0·0026; unified scale (^{12}C = 12) 107·8694 ± 0·0026.

The uncertainties indicated with these figures are the 95% confidence limits for the random errors added to estimates of possible systematic errors. These results are in very close agreement with recent American work and differ significantly from the present internationally accepted values.

It has been shown that the mass discrimination in the mass spectrometers used is dependent on the magnitude of the isotopic ratio. When an electron multiplier is used the correction due to the differing isotopic masses of the ions accelerated to the same energy (approximately 8 kv) is directly proportional to the ratio of the square root of the masses with an accuracy of 4 parts in 10,000.

Natural silver is composed of two stable isotopes $^{107}_{47}Ag$ and $^{109}_{47}Ag$ and we observed that the ratio of the first to the second of these two isotopes in natural silver appeared to be 1·084 ± 0·002 * which did not agree with the generally accepted value of 1·055 ± 0·003 due to White and Cameron.[1] These authors did not claim a greater accuracy than ±1%, but they attempted to reduce systematic errors and used two different, though physically similar, mass-spectrometers for the measurements.

The atomic weight of silver calculated from the isotopic abundance ratio when the isotopic masses are accurately known is a standard of such an importance in the determination of atomic weight,[2] and in the definition of practical electrical units, that a resolution of the differences was necessary, especially as earlier measurements of the abundance ratio were nearer to 1·084 than to 1·055. For instance, Paul [3] found 1·080 ± 0·006 and Hess, Marshall, and Urey [4] later found 1·0825 ± 0·0018 (the limits have been calculated from the published results by assuming that mean deviation = 0·798 standard deviation).

Accordingly samples of silver were chosen, two of early date and thus composed of silver from the Old World sources,[5] the others of recent date containing silver from modern sources and subject to such isotopic fractionation as occurs in electrolytic refining. Their isotopic abundance ratios were expected to reflect the differences that would arise in the random selection of silver in a laboratory reagent.

There was another source of error to be investigated arising from the method used to obtain a positive-ion beam in the mass-spectrometer. In White and Cameron's work positive silver ions were obtained by electron bombardment of silver chloride vapour. In our work a thermal ionization process of relatively high efficiency has been used in

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* All important figures in this paper are accompanied by their standard deviations, unless the contrary is stated.

[1] White and Cameron, *Phys. Rev.*, 1948, 991; Bainbridge and Nier, " Relative Isotopic Abundances of the Elements," Prelim. Report 9, Nuclear Science Series, Nat. Res. Council, Washington D.C., 1950; Stehn and Clancy, " Chart of the Nuclides," Knolls Atomic Power Laboratory, G.E. Company of America, 1956.

[2] Eméleus and Anderson, " Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul Ltd., London, 3rd edn., 1960, p. 37.

[3] Paul, *Z. Physik.* 1948, **124**, 244; *Naturwiss.*, 1943, **31**, 419.

[4] Hess, Marshall, and Urey, *Science*, 1957, **126**, 1291.

[5] Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1946, Vol. III, p. 298.

which tungstic oxide with a very high work function [6] is formed upon a tungsten filament, the alkali-metal poisons being removed as complex ions. It seemed possible that diffusion in such an ion source might be responsible for the discrepancies between different observations, since Hess, Marshall, and Urey used a very similar process. Therefore, we have kept under observation changes in the abundance ratio during the life of the ion source and have used more sensitive instruments than that originally employed. This greater sensitivity has been achieved by using electron-multiplier ion detectors which have long been known [7a, 7d, 8] to respond according to the ion velocity.

Ploch and Walcher [7d] showed that singly charged ions of different isotopes of the same element, when given the same velocity, caused secondary electron emissions within 1% of the same intensity. This holds for the energy range 600—6000 v and the elements lithium, neon, and potassium. Higatsberger *et al.*[8] likewise found that, for the same energy (in the range 1000—6000 v), isotopic ions gave secondary emissions which were inversely proportional to the mass of the isotopes. In our work, the energy of the silver ions hitting the first dynode of the electron multiplier was about 8000 v and was held constant during a mass analysis. Thus for an element consisting of two isotopes of masses m_1 and m_2, the ions of each being accelerated through a potential difference of E volts, the velocities v_1 and v_2 would be given by $Ee = \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$, or $v_1/v_2 = \sqrt{(m_2/m_1)}$. The correction factor to be applied to the ratio (Abundance of isotope 1)/(Abundance of isotope 2), found by means of an electron multiplier detector, would then be $\sqrt{(m_1/m_2)}$. We have sought accurately to substantiate this correction.

In order to establish the absolute ratio of the two isotopes in natural silver it is necessary to find the magnitude of mass-discrimination in the mass-spectrometer. Ideally this would be done by mixing known quantities of the pure isotopes and then finding the isotopic abundance ratio in the mass spectrometer. In practice the pure isotopes of silver are not available and silver enriched in each isotope must be used. Furthermore, in order to be certain of the quantities used in making the mixtures, the metallic silver must be chemically pure when weighed.

A preliminary publication of our results [9] led Shields, Craig, and Dibeler [10] very generously to let us have their own results which were then complete. This enabled us specifically to test an assumption made by them, namely, that the mass-distribution or " bias " of a mass-spectrometer is independent of the absolute value of the isotopic abundance ratio.

EXPERIMENTAL

Instruments.—Two similar mass-spectrometers were used, both instruments of 12 in. radius and with 90° magnetic deflection, of Type M.S.5 built by A.E.I. Ltd., Instrumentation Division. They produced ion beams by means of a triple-filament thermal-ionisation source [11] which could be used as a single-filament source when necessary. The ion beams were detected and measured with an electron multiplier, the output of which was applied to a high resistance (10^9 ohms), the voltage developed on this load being measured by means of a D.C. amplifying electrometer feeding a recorder which made permanent records of the measurements. For ion-currents greater than 10^{-14} amp. the ion beam was applied directly to another high resistance (4×10^{10} ohms), and the voltage on this was recorded by means of another electrometer and recorder. Voltages in the range 50 mv to 10 v were measured in this way. The linearity and accuracy of the measuring system were checked frequently by applying known voltages (accuracy ± 10 μv) to the system and observing the response. To guard against the effect of any voltage coefficient in the load resistors, No. 1 machine was used in the form supplied by the maker with English-made load resistors reputed to be subject to very small voltage

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[6] Crouch, unpublished work; Joint Conference on Mass Spectrometry, Oxford, Sept., 1961.

[7] Duckworth, " Mass Spectroscopy," Cambridge Univ. Press, 1958, pp. (*a*) 55, (*b*) 179, (*c*) 111, (*d*) 255.

[8] Higatsberger, Demorest, and Nier, *J. Appl. Phys.*, 1954, **25**, 883.

[9] Crouch, Preece, Swainbank, and Turnbull, *Nature*, 1959, **184** (Suppl. No. 4683), p. 358.

[10] Shields, Craig, and Dibeler, *J. Amer. Chem. Soc.*, 1960, **82**, 5033.

[11] Palmer, " Advances in Mass Spectrometry," Pergamon, London, 1959, p. 89.

coefficients, and No. 2 machine was equipped with American-made load resistors reputed to have very low voltage coefficients indeed. No. 2 machine also differed slightly in the electrostatic focusing arrangements in the ion-source.

Ionisation Technique.[6]—The tungsten filaments in the ion-source [11] were 0·030 in. wide and 0·001 in. thick. Approximately 20 μg. (or less) of silver were applied to the centre filament in 10 μl. of solution N in nitric acid, by means of an ultramicro-pipette, the delivery being watched by means of a binocular microscope. After every application current was passed through the filament to evaporate the water and acid. All the silver occupied less than 3 mm. at the centre of the filament. After all the silver had been mounted, 10 μl. of just ammoniacal saturated boric acid solution were then applied. When all the water had evaporated the residue was heated to expel all the water of crystallisation and finally just to melt the boric oxide.

The source was quickly transferred to the mass-spectrometer or kept over silica-gel until required. In the mass-spectrometer, with the pressure reduced to normal, the centre filament was heated sufficiently to raise $^{39}K^+$ beams. Rb^+ beams were then located at a slightly higher temperature and, when these had been increased to 10^{-13} amp., beams of $Na_2BO_2^+$ at mass numbers 88 and 89 became evident. These were raised to 10^{-14} amp. and $KNaBO_2^+$ beams were located at mass numbers 104, 105, 106, and 107. Slowly these were raised to $\sim 10^{-14}$ amp. after which they gradually disappeared, leaving small beams at mass numbers 107, 108, and 109. Finally, when the Ag^+ beams appeared they were increased by a very gradual raising of the filament current. Measurements were made of the relative intensity of the $^{107}Ag^+$ and the $^{109}Ag^+$ beams, care being taken to resolve the satellite peaks at mass numbers 107, 108, and 109. These disappeared when the Ag^+ beams reached 10^{-13} amp. although in mixtures where one isotope greatly preponderated it was essential to monitor the satellite peaks throughout the analysis. The satellites are associated with the boron oxides remaining on the centre filament, and they differ in mass from the $^{107}Ag^+$ and $^{109}Ag^+$ to such an extent that they are resolvable on the machines used which possess mass-dispersions of $M/\Delta M > 300$ and abundance resolutions of $<10^{-4}$, *i.e.*, the contribution at the next mass-number from the "tail" of a beam at a given mass number is less than 10^{-4} of the beam.

Preparation of Known Mixtures of Enriched Isotopes.—Approximately 100 mg. of silver enriched in each of the stable isotopes of silver were available in the form of metallic foil. It was necessary to purify the silver so that it could be accurately weighed. All the apparatus used was of fused silica, except where noted; it was left in concentrated nitric acid overnight and kept in deionised water until required; then it was washed with deionised water which had been distilled in an all-silica apparatus.

The nitric acid had been twice distilled in silica apparatus and was kept in a flask of fused silica. Ammonia solutions were made by dissolving gaseous ammonia in deionised, distilled water and kept in Polythene bottles. Hydrochloric acid solutions were prepared by dissolving hydrogen chloride in deionised, distilled water and were also kept in Polythene bottles.

The isotopically enriched metallic silver was fused on blocks of lime (analytical reagent grade) in the flame of an oxy-coal gas torch; the metal bead was dissolved in concentrated nitric acid, and the solution diluted to 20 ml., ~2N in nitric acid, in a fused-silica centrifuge tube. The silver was precipitated by dropwise addition of 6N-hydrochloric acid to the warm solution, then centrifuged to the bottom of the tube, and the supernatant liquid was removed with a transfer pipette. The solid was dissolved in the minimum quantity of concentrated ammonia, diluted to 20 ml. with water, any trace of residue was removed by centrifuging, and the chloride was reprecipitated with 6N-hydrochloric acid. After being washed with water the precipitate was redissolved in the minimum quantity of 6N-ammonia in a centrifuge tube, the solution was diluted to 20 ml. and hydrogen sulphide was passed through it. The silver sulphide was recovered by centrifugation and removal of the supernatant solution; it was washed with water and again centrifuged. The sulphide was treated in warm 6N-nitric acid; this deposited and coagulated the sulphur, and the silver in solution was readily recovered by means of a pipette, after centrifugation. The solution was evaporated to dryness and the silver nitrate dissolved in 5 ml. of 2N-nitric acid and transferred to a 10-ml. borosilicate-glass beaker. This vessel had been kept in concentrated nitric acid for several days and then been stored in pure water. Three treated beakers, half-filled with 2N-nitric acid, were set in line with the first, and the four beakers were connected in series by capillary bridges of borosilicate-glass tube filled with 2N-nitric acid. A platinum-foil cathode of about 1 cm.^{2} area was put in the silver solution and a similar anode in the fourth beaker. Most of the silver was deposited in crystalline form by a direct current of 8—40 milliamp. per cm.^{2} of cathode. The cathode was removed without the current's being switched off and was washed by immersion in several changes of water followed by a jet of water. It was dried at 110° in an electric air-oven. The silver crystals were easily detached by tapping the cathode and by brushing it with a camel-hair brush. They were melted in a silica tube, first under oxygen and then under nitrogen, to a bead which was pickled in 10% sulphuric acid (analytical grade) and then in warm 10% hydrofluoric acid contained in a " lusteroid " centrifuge tube until examination by means of a binocular microscope showed complete removal of a few very small surface inclusions from the metal. The bead was washed in pure water, dried at 110° in air, and weighed.

It was placed in a weighed, graduated, borosilicate-glass flask and dissolved by slow addition of concentrated nitric acid and the solution was diluted to the mark with water. The flask and contents were then weighed. Samples of the silver solution were taken next norning for spectrographic analysis. Experiments showed that solutions weighed in sealed Polythene containers, previously soaked in water for 24 hr., showed inappreciable loss by evaporation. In two cases mixtures were made with natural silver (from Johnson Matthey and Co. Ltd.) as one component. This was pickled in 10% hydrofluoric acid, washed with deionised, distilled water, and dried at 110° in an electric oven.

Natural Silver Samples used to Determine the Ratio ^{107}Ag/^{109}Ag.—The sample designated Natural Silver No. 1 was removed from a piece of silver plate bearing the Sheffield hall-mark for 1899. Natural Silver No. 2 was from plate with the London hall-mark for 1791. Natural Silver No. 3 was from plate with the London hall-mark for 1959. Natural Silver No. 4 was Johnson Matthey's " Specpure " material, but was not identical with that used in the preparation of the isotopically enriched mixtures. Natural Silver Nos. 5 and 6 were from silver nitrate reagent bottles containing standardised solutions.

Determination of the ^{107}Ag/^{109}Ag *Ratio*.—After the ^{107}Ag and the ^{109}Ag beams had been located in the mass-spectrometer with the aid of the electron multiplier, they were gradually increased, measurements were then made and, finally, the ion-beams were collected directly and more measurements were made. The measurements were recorded as peaks on the recorder chart (beam intensity *versus* time), in groups of five consecutive pairs. Thus, at a given ion-beam intensity, data became available from which $5n$ ratios could be determined (n being a positive integer). At the end of the mass analysis, the data were fed into a Ferranti Mercury computer programmed to obtain the mean and its standard deviation for every set of five consecutive ratios, and the overall mean, and its standard deviation for all the ratios found with the electron multiplier, together with similar results obtained from direct ion-beam collection. The means of the groups of five consecutive ratios were then plotted so that systematic variation of the ratio throughout the life of the source could be detected. As the computer was not used for the results from some of the earlier samples, a few of the results are not exactly in this form.

Experimental Findings.—Table 1 contains the quantities of isotopically enriched silver metal which were combined to form the mixtures, the isotope ratios of which are given in subsequent Tables 2—7). The figures in parentheses after the isotopic ratios in the Tables indicate the number of ratios which were combined to give the result.

TABLE 1.

Quantities of isotopically enriched silver metal used in the preparation of the mixtures.

^{107}Ag enriched pure metal bead = 24·53 ± 0·02 mg.
^{109}Ag ,, ,, = 79·59 ± 0·02 mg.
Natural silver metal grain = 87·70 ± 0·02 mg.

^{107}Ag enriched silver solution (solution A) = 10·2701 g.
^{109}Ag ,, ,, (solution B) = 25·3203 g.
Natural silver solution (solution C) = 25·9408 g.

Constituents of mixtures

Mixture	Solution A (g.)	Solution B (g.)	Solution C (g.)	Mixture	Solution A (g.)	Solution B (g.)	Solution C (g.)
1	Solution A only			5	Solution B only		
2	3·8396	1·0443	—	6	—	2·0104	0·9976
3	1·3851	1·0600	—	7	—	1·9836	0·4832
4	1·0016	1·9786	—				

TABLE 2.

Spectrographic analysis of the purified isotopically enriched silver solutions. Impurities (% by wt.) in silver metal.

	Na	Ca	Pt	Fe	Al	Cu	Mg	Si
^{107}Ag solution	0·049	0·01	0·004	<0·003	<0·004	<0·001	<0·0008	<0·001
^{109}Ag solution	0·022	0·008	0·007	<0·002	<0·003	<0·0006	<0·001	<0·001

The following elements were sought but were not detected: Li, Ba, K, Cs, Rb, Sr, As, Be, Au, B, Bi, Cd, Cr, Ge, In, Mn, Mo, Ni, Pb, P, Sb, Sn, Ti, Tl, V, W, Zn, Co, Pd, Sc, Hg, La, Ir, Ga, Os, Nb, Y, Rh, Zr, Ru.

A second sample taken after further storage in the glass standard flasks gave the following results for sodium, expressed as Na% by wt. in Ag: ^{107}Ag solution 0·049; ^{109}Ag solution 1·2.

TABLE 3.

Spectrographic analysis of the natural silver grain used in the preparation of mixtures. Impurities (% by wt.) in silver metal.

Zn, 0·0002; Fe, 0·0001; Cu, <0·0001; Mg, <0·0001.

The following elements were sought but not detected: Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cs, Ga, Ge, Hf, In, Ir, K, Li, Mn, Mo, Na, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Sc, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zr.

TABLE 4.

Comparison of the ^{107}Ag/^{109}Ag ratios found on natural silver samples by using No. 1 machine.

Natural silver sample	Ratio using multiplier (1)	Ratio using direct collection (2)	Ratio (1)/(2)
No. 1	1·0938 ± 0·0023 (50)	1·0833 ± 0·00046 (29)	1·0097 ± 0·0022
No. 2	1·0961 ± 0·0014 (50)	1·0831 ± 0·0031 (10)	1·0119 ± 0·0036
No. 3	1·0940 ± 0·0020 (60)	1·0827 ± 0·0010 (45)	1·0105 ± 0·0021
No. 4	1·0963 ± 0·0016 (125)	1·0877 ± 0·0026 (35)	1·0079 ± 0·0027
Mean	1·09527 ± 0·00082	1·08419 ± 0·00093	1·01000 ± 0·00264

Overall mean ^{107}Ag/^{109}Ag ratio [assuming ratio (1)/(2) = 1·0093]: 1·0849 ± 0·0009.

TABLE 5.

Comparison of the ^{107}Ag/^{109}Ag ratios found in mixtures 1—7 by using No. 1 machine.

Mixture	Ratio found using the multiplier (1)	Ratio found using direct ion-beam collection (2)	Ratio (1)/(2)
1	65·359 ± 0·059 (50)	—	—
2	2·7810 ± 0·0041 (85)	—	—
3	1·0127 ± 0·0012 (95)	0·9995 ± 0·0009 (10)	1·0132 ± 0·0012
4	0·39998 ± 0·00070 (100)	0·39489 ± 0·00126 (10)	1·0117 ± 0·0010
5	0·0081514 ± 0·0000141 (50)	—	—
6	0·23342 ± 0·00027 (95)	—	—
7	0·13092 ± 0·00013 (95)	0·13065 ± 0·00096 (10)	1·0021 ± 0·0060
		Mean ratio (1)/(2) =	1·0090 ± 0·0034

TABLE 6.

Comparison of ^{107}Ag/^{109}Ag ratios found on natural silver samples by using No. 2 machine.

Natural silver sample	Ratio using multiplier (1)	Ratio using direct collection (2)	Ratio (1)/(2)
1	1·09236 ± 0·00059 (85)	1·08345 ± 0·00110 (35)	1·00822 ± 0·00122
2	1·09498 ± 0·00062 (60)	1·08433 ± 0·00055 (50)	1·00982 ± 0·00078
3	1·09365 ± 0·00058 (85)	1·08243 ± 0·00066 (45)	1·01037 ± 0·00083
4	1·09325 ± 0·00060 (60)	1·08453 ± 0·00069 (45)	1·00804 ± 0·00087
5	1·09462 ± 0·00110 (40)	1·08515 ± 0·00159 (25)	1·00873 ± 0·00188
6	1·09240 ± 0·00075(50)	1·08207 ± 0·00071 (30)	1·00955 ± 0·00097
Mean	1·09351 ± 0·00028	1·08366 ± 0·00035	1·0091 ± 0·0004

TABLE 7.

Comparison of the $^{107}Ag/^{109}Ag$ ratios found by using the electron multiplier with those found by using direct ion-beam collection on mixtures 1 to 7; No. 2 machine.

Mixture	Ratio found using the electron multiplier (1)	Ratio found using direct ion-beam collection (2)	Ratio (1)/(2) with standard deviation	
1	64·697 ± 0·119 (95)	64·752 ± 0·136 (30)	0·9992 ± 0·0174	Mean 1·0098 ± 0·0054
	65·897 ± 0·087 (55)	64·817 ± 0·173 (50)	1·0167 ± 0·0217	
	66·493 ± 0·068 (75)	65·610 ± 0·196 (25)	1·0135 ± 0·0244	
2	2·7769 ± 0·0047 (85)	2·7623 ± 0·0032 (105)	1·0053 ± 0·0026	
3	1·0117 ± 0·0007 (175)	1·0011 ± 0·0008 (25)	1·0105 ± 0·0011	
4	0·3982 ± 0·0003 (190)	0·3925 ± 0·0005 (95)	1·0145 ± 0·0013	
5	0·007860 ± 0·000033 (35)	0·007730 ± 0·000051 (45)	1·0168 ± 0·0043	Mean 1·0178 ± 0·004
	0·007865 ± 0·000007 (50)	0·007720 ± 0·000096 (10)	1·0189 ± 0·0014	
6	0·2342 ± 0·0008 (75)	0·2293 ± 0·0005 (15)	1·0216 ± 0·0038	
7	0·1290 ± 0·0008 (140)	0·1277 ± 0·0004 (90)	1·0100 ± 0·0033	

DISCUSSION

An accurate atomic weight of a naturally occurring element has little interest unless there is a reasonable certainty of constancy in the isotopic abundances of the element from diverse sources. Shields *et al.*[10] have examined native silver from several American mines and have concluded that any variation there may be in the $^{107}Ag/^{109}Ag$ ratio is less than 0·2% of the ratio, although they mention one sample as being outside this limit. They intend [12] to extend their investigations and to re-examine this sample.

Our results summarised in Tables 4 and 6 bear out their findings. For example, the analysis of variance of the data summarised in Table 6 shows that differences of about 0·3% would have been detected between the mean ratios found by using the multiplier detector for each of the natural silver samples. About the same difference would have been detected between the ratios found by direct ion-beam collection.

There were available about 100 mg. of silver enriched in each of the stable isotopes and our method of purification was similar to that used by Shields *et al.*[10] modified to suit the much smaller quantities. Their purity was established by analysing the solutions of the dissolved metal beads, but only limited quantities could be spared for the analysis and the limits of impurity given in Table 2 reflect this. It is reasonable to suppose that the sodium and calcium were not contained in the silver but were derived from the glass containers despite the rigorous treatment they had received. In evidence of this a second sample analysed one week after the first showed much more sodium, although the water and acid which had been used did not contain measurable quantities of the element. But if all the impurities are to be attributed to the metallic silver it will be shown that their effect is very small, and that it has been allowed for in the calculation of possible errors.

Measurements made with the two mass-spectrometers will be discussed separately since the results from No. 1 were all made before No. 2 was built.

The isotopic abundance ratios of natural silver samples obtained on No. 1 machine are summarised in Table 4. There are no significant differences between the mean values obtained with the aid of the electron-multiplier detector, or between those obtained by direct ion-beam collection. Further, the ratio between the mean of values found with the multiplier and those from direct ion beam collection should be equal to

$$\left(\frac{\text{Atomic mass of } ^{109}\text{Ag}}{\text{Atomic mass of } ^{107}\text{Ag}}\right)^{\frac{1}{2}} = 1{\cdot}0093 \text{ according to Duckworth's data.}^{7b}$$

Our experimental value is 1·0100 ± 0·0026 which agrees within experimental error and justifies a use of the correction factor 1/1·0093 even in those instances where the isotope ratio was so great that only few measurements with direct ion-beam collection could be

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[12] Shields, Garner, and Dibeler, personal communication.

made before exhaustion of the source. Table 5 gives the ratios found for mixtures 1—7, the compositions of which are given in Table 1.

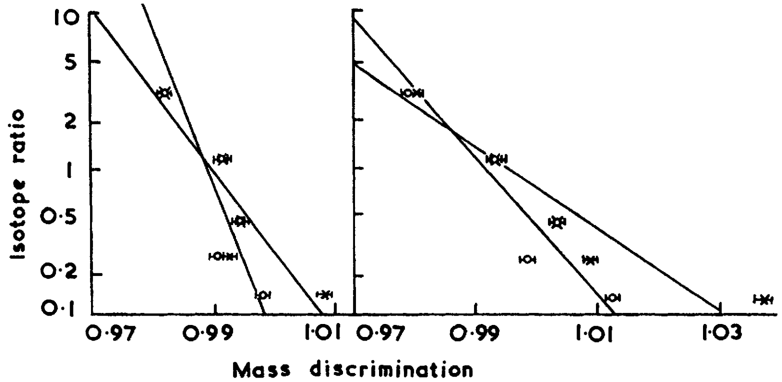
If D and S are respectively the weights of ^{107}Ag-enriched silver and ^{109}Ag-enriched silver, used to prepare a given mixture, and if D_0, S_0, and M_0 are, respectively, the observed $^{107}\mathrm{Ag}/^{109}\mathrm{Ag}$ ratios found for the ^{107}Ag-enriched silver, the ^{109}Ag-enriched silver, and the mixture, then the mass discrimination δ defined by the ratio

$$\delta = \frac{\text{True abundance ratio } ^{107}\mathrm{Ag}/^{109}\mathrm{Ag}}{\text{Observed abundance ratio } ^{107}\mathrm{Ag}/^{109}\mathrm{Ag}}$$

is given by:[13]

$$\delta = \frac{1 - \dfrac{D}{S}\left(\dfrac{M_0 - D_0}{S_0 - M_0}\right)}{W\left[S_0\left(\dfrac{M_0 - D_0}{S_0 - M_0}\right)\dfrac{D}{S} - D_0\right]} \qquad (1)$$

where W is the ratio (Atomic mass of ^{107}Ag)/(Atomic mass of ^{109}Ag), and it is assumed (with Shields *et al.*[10]) that the mass discrimination is independent of the absolute values of the isotopic abundance ratios. Insertion of the mean of the ratios obtained for mixtures 2, 3, 4, 6, and 7 with the multiplier detector, corrected by the factor 1/1·0093, and the relative quantities of isotopically enriched silver samples used in these mixtures, leads to five estimates of δ. These estimates were not equal and, when plotted against the logarithm of the observed isotopic abundance ratio for the mixtures, gave a reasonably straight line (Fig. 1). Accordingly it was necessary to find the nature of the dependence of the mass discrimination on the abundance ratio. If the true value of D_0 and S_0 were D_0' and S_0', respectively, then for a mixture the $^{107}\mathrm{Ag}/^{109}\mathrm{Ag}$ ratio of which is observed to be M_0,



Mass discrimination as a function of isotope ratio.

FIG. 1. No. 1 machine. FIG. 2. No. 2 machine.

✱ 1st approximation; –O– 4th approximation.

$$\delta = \frac{D_0'\dfrac{D}{S}\left(\dfrac{S_0'W + 1}{D_0'W + 1}\right) + S_0'}{M_0\dfrac{D}{S}\left(\dfrac{S_0'W + 1}{D_0'W + 1}\right) + 1} \qquad (2)$$

From the straight-line relationship between δ and $\log M_0$ obtained by equation (1) and the results obtained from mixtures 2, 3, 4, 6, and 7, values for the mass-discrimination were read off and used to obtain approximations to D_0' and S_0'. The introduction of these approximations in expression (2) for the mixtures 2, 3, 4, 6, and 7 led to a second

[13] Crouch and Webster, unpublished work.

series of values for the mass-discrimination corresponding to the observed isotope abundance ratios. This series was fitted by the method of least squares with a straight line connecting the logarithm of the ratio and the corresponding value of the mass-discrimination. This line was used to obtain values for the mass-discriminations corresponding to D_0 and S_0 and thus to derive better approximations to D_0' and S_0'. This process was repeated and after four successive approximations the values of D_0' and S_0' showed no change. The relation between the logarithm of the isotopic abundance ratio and the corresponding mass-discrimination was

$$\delta = 0{\cdot}9894 - 0{\cdot}0092 \log R,$$

where R is the isotopic abundance ratio corresponding to δ. This line is plotted in Fig. 1 with the fourth approximations to the values of the mass discrimination at the isotopes ratios appropriate to mixtures 2, 3, 4, 6, and 7.

Thus at $R = 1{\cdot}0849 \pm 0{\cdot}0009$, $\delta = 0{\cdot}9891 \pm 0{\cdot}0018$ and the absolute value of the natural silver isotopic abundance ratio $^{107}\mathrm{Ag}/^{109}\mathrm{Ag} = 1{\cdot}0731 \pm 0{\cdot}0022$. The standard deviation quoted with the mass-discrimination was deduced from the scatter of the fourth approximations about the best-fitting line as plotted in Fig. 1, and includes the effect of all random errors. It does not include a possible bias due to errors in the value of D/S consequent upon impurity in the silver beads, or the error in their weighing. Supposing the purified isotopically enriched metallic beads to contain all the impurities listed in Table 2 to the maximum quantities, *i.e.*, that the ^{107}Ag-enriched metal was 99·93% pure, and the ^{109}Ag-enriched metal was 99·95% pure, then the ratios D/S would be biassed by 2 parts in 10,000, and in the worst case where the ^{107}Ag-enriched metal contained impurities and the ^{109}Ag-enriched metal did not, the bias would be 7 parts in 10,000. The values of M_0, S_0, and D_0 were, however, considerably more in error than this, their standard deviations being up to ten times greater; so that the " impurity " bias and that due to error in weighing, which is of the same magnitude, would have a negligible effect on the estimate of δ. The overall bias is believed to be 5 parts in 10,000.

The absolute value of the ratio $^{107}\mathrm{Ag}/^{109}\mathrm{Ag}$ for natural silver from No. 1 machine agrees, within the experimental errors, with that of Shields *et al.*[10] However, we used an electron-multiplier detector which might have given rise to dependence of mass discrimination on the isotope ratio, since the correction factor 1/1·0093 was used for all ratios. It is possible that the correction factor depended on the isotope ratio.

A further set of measurements, made on the same silver samples in another mass-spectrometer with care to obtain ratios by direct ion-beam collection as well as by means of the multiplier detector for all values of the abundance ratio, gave the results in Tables 6 and 7. The mean values from the electron multiplier and by direct ion-beam collection, were in close agreement with those obtained with No. 1 machine. The measurements we have made with both the mass spectrometers, which ran into several thousands, cannot be given in detail. They are in groups of five ratios, the results for the groups being obtained under apparently steady conditions during the stepwise increase of the ion emission. When the mean and the standard deviations of these groups are plotted as a time sequence, it is clear that they are independent of the beam size at any time; indeed the ratio appears to move at random round the overall mean value; but the rate of this change is slow compared with the time taken to obtain a group of five ratios (about 5 min.). This behaviour will be illustrated in detail in another place.[6] In order to obtain an overall mean ratio which reflects all the changes in the emission it seems to be necessary to include measurements taken during several hours of ion-emission. Alternatively, fewer ratios obtained from each of several different sources prepared from the same specimen might be expected to give the same result.

From the results in Table 6, the ratio between the abundance ratios found with the multiplier and by direct collection is $1{\cdot}0091 \pm 0{\cdot}0004$; thus the multiplier-detector correction factor, calculated to be the square root of the ratio of the atomic masses, is found to be correct within 4 parts in 10,000. The results in Table 7 have not been used in this calculation because they include figures for materials with very high or very low ^{107}Ag/^{109}Ag ratios. It happens that the time for which the source can be run during direct ion-beam collection is very limited, so that the mean ratios thus obtained may not reflect the long-term instability of the source. In general, the standard deviations of the ratios (1)/(2) in Table 6 are lower than those in Table 7 and, for this reason, only results in Table 6 have been used in the calculation of the multiplier correction factor. However, when the figures in the last columns of Tables 6 and 7 are plotted against the ratios ^{107}Ag/^{109}Ag there is no evidence of a systematic dependence of the multiplier correction on the ratio being measured. Results obtained only by direct ion-beam collection give a relation between mass discrimination and isotope-abundance ratio similar to that for No. 1 machine (Fig. 2), namely, $\delta = 0{\cdot}9913 - 0{\cdot}0224 \log R$. This dependence is far larger than can be accounted for by a difference in the ionisation potential of the isotopes, since measurements of the isotope shift in the vicinity of silver in the Periodic Table show this difference to be very small (see, for example, the measurements on palladium [14]); it is believed that the explanation lies in the discriminatory effects of the ion-source focusing arrangements, and there is other evidence to support the explanation.[13]

For No. 2 machine $R = 1{\cdot}08366 \pm 0{\cdot}00035$, $\delta = 0{\cdot}9905 \pm 0{\cdot}0023$, and the absolute value of the natural-silver isotopic abundance ratio ^{107}Ag/^{109}Ag $= 1{\cdot}0734 \pm 0{\cdot}0026$; this agrees with the result obtained from No. 1 machine, and both values are consistent with the results of Shields *et al.*[10]

Taken together, the two values for the ^{107}Ag/^{109}Ag abundance ratio give a mean value of $1{\cdot}0733 \pm 0{\cdot}0012$. This may be subject to a bias of $\pm 0{\cdot}0005$ due to errors in the weighing or deviations from purity. The most probable absolute isotopic abundance ratio is $1{\cdot}0733 \pm 0{\cdot}0043$, based on 95% confidence limits added to an estimate of the possible bias. This gives for the atomic abundances estimates of ^{107}Ag $51{\cdot}765 \pm 0{\cdot}028$ atom % and of ^{109}Ag $48{\cdot}235 \pm 0{\cdot}028$ atom %, with possible biases of 0·012%. There is good reason to follow Shields *et al.*[10] and use the atomic mass measurements of Johnson and Nier for ^{107}Ag ($106{\cdot}93899 \pm 0{\cdot}00010$) and ^{109}Ag ($108{\cdot}93928 \pm 0{\cdot}00010$) ($^{16}\mathrm{O} = 16$), the uncertainties being possible biases. Then the physical-scale atomic weight of silver is

$$\frac{1}{100}[(51{\cdot}765 \pm 0{\cdot}028)106{\cdot}93899 + (100 - 51{\cdot}765 \pm 0{\cdot}028)108{\cdot}939]$$

$$= \frac{1}{100}[10{,}895{\cdot}928 - (51{\cdot}765 \pm 0{\cdot}028)2{\cdot}00029]$$

$$= 107{\cdot}90373 \pm 0{\cdot}00055 \ (^{16}\mathrm{O} = 16).$$

This has a possible bias of 0·00034, so that the total uncertainty based on 95% confidence limits is $0{\cdot}002299 \pm 0{\cdot}00034 = 0{\cdot}0026$, which makes our value for the atomic weight of natural silver $107{\cdot}9037 \pm 0{\cdot}0026$ ($^{16}\mathrm{O} = 16$).

The factor $1{\cdot}000275 \pm 0{\cdot}000007$ (Nier,[15] quoted by Shields *et al.*[10] and Duckworth [7c]) applied to the physical-scale gives the chemical-scale atomic weight as $\dfrac{107{\cdot}9037 \pm 0{\cdot}0026}{1{\cdot}000275 \pm 0{\cdot}000007} = 107{\cdot}8740 \pm 0{\cdot}0033$ (O = 16), the uncertainty in the conversion factor having been treated as a possible bias. This value differs significantly from that internationally accepted,[17] *viz.*, 107·880 (O = 16), but it agrees well with the recent independent determination by Shields, Craig, and Dibeler,[10] *viz.*, $107{\cdot}8731 \pm 0{\cdot}0020$ (O = 16).

On the unified chemical and physical scale [16] the atomic weight of silver becomes $\dfrac{107{\cdot}9037 \pm 0{\cdot}0026}{1{\cdot}000317917} = 107{\cdot}8694 \pm 0{\cdot}0026$ ($^{12}\mathrm{C} = 12$).

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[14] Hughes and Sharpton, *Phys. Rev.*, 1961, [ii], **121**, 1702.

[15] Nier, *Phys. Rev.*, 1950, **77**, 789.

[16] Mattauch, *J. Amer. Chem. Soc.*, 1958, **80**, 4125.

[17] Report of the Commission on Atomic Weights, I.U.P.A.C. 19th Conference, 1957.

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CHEMISTRY DIVISION, A.E.R.E.,
HARWELL, DIDCOT, BERKS.

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