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Absolute Isotopic Abundance Ratio and the Atomic Weight of Chlorine

BY WILLIAM R. SHIELDS, THOMAS J. MURPHY, ERNEST L. GARNER AND VERNON H. DIBELER

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An absolute value is obtained for the isotopic abundance ratio of natural chlorine by surface emission mass spectrometry and by the use of calibration samples of known isotopic composition prepared from nearly pure separated chlorine isotopes. Mass Spectrometric data obtained on two instruments result in an absolute value for the ratio, $Cl^{35}/Cl^{37} = 3.1272 {}^{+0.0079}_{-0.0082}$. Previous workers have observed no variation in isotopic abundance greater than 0.1% of the isotope ratio among naturally occurring materials and minerals. The calculated atomic weight of chlorine on the recently proposed unified physical and chemical atomic weight scale ($C^{12} = 12$) is $35.45273 {}^{+0.00092}_{-0.00097}$. The indicated uncertainties are over-all limits of error based on 95% confidence limits for the mean and on allowances for effects of known sources of possible systematic error. Mass spectrometric determinations of the atomic weights of chlorine and silver give a combining weight ratio, Cl/Ag = 0.328667.

Introduction

Mass spectrometric determination[1,2] of the absolute isotope abundance ratio for natural silver using mixtures of separated isotopes for instrument calibration have resulted in a value of 107.8682 ± 0.0010 ($C^{12} = 12$) or 107.8729 ± 0.0010 (O = 16); significantly different from the value, 107.880 (O = 16) as previously accepted by the International Committee on Atomic Weights.[3] Recently, a similar measurement by British workers[4] has given a concordant result.

Silver is one of the key elements in chemical determinations of atomic weight and in conjunction with the halogens, particularly chlorine and bromine, forms the classical basis for establishing the atomic weights of many of the elements. Combining weight measurements of silver and halogens represent some of the most precise relative weight measurements known to date. A considerable body of these data for the chlorine–silver ratio has accumulated in the last 50 years. Representative of this work are the early measurements by Richards and Wells.[5] They report the ratio Cl/Ag = 0.32867 with a probable error of 0.0005. However, pooling the recorded data of these and other workers results in a value of 0.328667 with a very small probable error.[6] Thus an accurate determination of the atomic weight of chlorine together with the previous physical determination of the atomic weight of silver provides an independent means of establishing this fundamental ratio and also of supporting the physical determination of the atomic weight of silver.

Only a few measurements of the isotopic abundance of chlorine have been reported. Bainbridge and Nier[7] examined the measurements prior to 1950 and adopted the values[8] $Cl^{35} = 75.4$ atom per cent and $Cl^{37} = 24.6$ atom per cent. Later Nier showed[9] that this value led to a chlorine atomic weight of 35.462 ± 0.008 (O = 16) with the uncertainty resulting principally from the measurement of the isotopic abundance. This is at considerable variance with the presently accepted atomic weight of 35.457(O = 16).[3] Two other electron impact measurements of chlorine isotope

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[1] W. R. Shields, D. N. Craig and V. H. Dibeler, *J. Am. Chem. Soc.*, **82**, 5033 (1960).

[2] W. R. Shields, E. L. Garner and V. H. Dibeler, *J. Research NBS*, **66A**, 1 (1962).

[3] E. Wichers, Report on the 1959 meeting of the International Commission on Atomic Weights, Comptes Rendus De La Vingtieme Conference de Chimie Pure et Appliquée, Munich, 1959.

[4] E. A. C. Crouch and A. H. Turnbull, private communication.

[5] T. W. Richards and R. C. Wells, Carnegie Institution of Washington, Publication No. 28, 1905.

[6] By private communication with E. Wichers and D. N. Craig.

[7] K. T. Bainbridge and A. O. Nier, "Relative Isotopic Abundance of the Elements: Preliminary Report No. 9, National Research Council, Washington, D. C.

[8] A. O. Nier and E. E. Hanson, *Phys. Rev.*, **50**, 722 (1936).

[9] A. O. Nier, *Science*, **121**, 737 (1955).

abundance report $Cl^{35} = 75.53\%$[10] and $Cl^{35} = 75.8\%$,[11] and one surface emission measurement reports[12] a mean natural abundance of $Cl^{35} = 75.3\%$. Recently, Meyerson[13] calculated the average Cl^{35} abundance from mass spectra of several chlorine-substituted hydrocarbons and obtained the value, $Cl^{35} = 75.80$ atom per cent. with an average deviation of 0.06%. This would give an approximate atomic weight of 35.454 (O = 16). Although some tests for instrumental discrimination were applied in each of the above cases, the conclusions concerning discrimination are equivocal. In the present work, this difficulty is obviated by the use of calibration samples of known isotopic composition prepared from nearly pure separated chlorine isotopes. Also, Hoering and Parker[14] recently reported no variation greater than 0.1% of the Cl^{35}/Cl^{37} ratio among 81 samples of natural occurrence. Some measurements are reported here on natural chlorine from mineral samples in order to confirm these observations, if possible.

Experimental

Instrumentation.—The surface emission mass spectrometers[1,2] used to compare the isotope abundance ratios of chlorine in the natural and commercial samples with those of the calibration samples are two nearly identical 12-inch radius-of-curvature, single focusing instruments with 68 degree analyser tubes and 60 degree magnet pole pieces. Each triple filament source used all-rhenium filaments 1 × 30 mils except while measuring the nearly pure separated isotopes. Then tungsten was employed for reasons given below. In general, the negative ion measurements were made under conditions similar to those of earlier positive ion measurements[1] except for electric and magnetic field reversals. However, certain critical conditions were noted. Satisfactory negative ion currents were obtained for a clean center filament operating nominally at 1550°. If halogens were deposited on the center filament, negative ion currents were immeasurably small until the temperature of the center filament was raised sufficiently to permit electron emission thus forming ions by electron bombardment. Chloride was deposited on the sample filaments in the form of ammoniacal solutions of silver chloride in conconcentrations of about 15 mg. Cl/ml. of solution. The use of alkali chlorides was abandoned as this form of the element gave very erratic results after several hours of operation and required frequent stringent cleaning of the ion source and collector assemblies.

Ion currents were measured by means of a vibrating reed electrometer with an expanded-scale recorder. Ion currents were nominally 10^{-12} ampere. Ratios were measured by varying the magnetic field at constant ion accelerating voltage.

Purification of the Separated Isotopes.—Electromagnetically separated chlorine isotopes in the form of sodium chloride were obtained from the Isotopes Division, Oak Ridge National Laboratory of the Union Carbide Nuclear Company. The $NaCl^{35}$ and $NaCl^{37}$ were designated: Series KL, Sample 1254 (a), and Series KL, Sample 1255 (a), respectively. The isotopes were chemically refined at ORNL by the reduction of the isotopic silver chlorides with hydrogen. Details of purification accompanying the samples indicated a high degree of cation purity but did not exclude the possible presence of other halogens. Thus the salts were further purified at NBS using facilities of the Applied Analytical Research Section to insure complete removal of bromide and iodide. Both separated isotope samples were treated as follows: The sodium chloride was dissolved in a small amount of water and transferred to a 300-ml. three-neck distilling flask and connected to a distilling apparatus like that described by Murphy, Clabaugh and Gilchrist.[15] The solution volume was increased to 90 ml. and 10 ml. of redistilled nitric acid was added. The solution was then refluxed for 2 hr. while a stream of halide-free air was drawn through the system. The heat was then increased and about 10 ml. of solution was distilled and set aside. Murphy, *et al.*, have shown[15] that this treatment reduced the concentration of any bromide or iodide originally present in the distilland to less than 10 p.p.m. The flask then was disconnected, 2 ml. of mercury was added and the solution was warmed until all of the chloride had precipitated as mercurous chloride. The solution was filtered with a fine porosity glass immersion filter and the residue in the flask was washed 5 times with distilled water. The chloride was recovered as sodium chloride by reduction of mercurous chloride with hydrogen peroxide in alkaline solution in the following procedure. About 50 ml. of water and solution containing 95% of the stoichiometric quantity of sodium carbonate were added to the flask. Two ml. of conc. ammonium hydroxide and 2 ml. of 30% hydrogen peroxide were added to the solution. After the reduction of $HgCl_2$ was complete, the resultant solution was filtered through a well washed Whatman No. 42 filter paper and evaporated to dryness in a platinum dish. The dish and contents were heated in an electric furnace for 2 hr. at 600° to volatilize any ammonium chloride produced in the reaction or any residual mercury. The salt was taken into solution with about 10 ml. of water and again filtered as above. The filtrate was caught in a 50-ml. glass-stoppered graduated flask and the dish and filter paper were washed with water until the volume was about 50 ml. The conversion of required amounts of the sodium chloride to silver chloride for isotopic analysis of the separated isotopes followed the simple procedure described later for the conversion of the calibration mixtures.

Chlorine Analysis of the Separate Isotope Solutions.—The chloride ion concentration in the solutions of the separated isotopes was measured by G. Marinenko of the Applied Analytical Research Section. Chloride ion was titrated with electrogenerated silver ions that were "metered" coulometrically. Samples of the purified separated isotope solutions were weighed directly into the titration cell using a semi-micro Ainsworth balance with an accuracy of ± 0.02 mg. and evaporated to a volume of about 5 ml. The cell walls were washed down with 45 ml. of a solution consisting of 2 *N* acetic acid, 1.7 *N* sodium nitrate and 40% methanol. The cell was covered with a rubber stopper containing the cathode compartment, generator electrodes and indicator electrodes. It was wrapped with aluminum foil to shield the contents from light and placed on a magnetic stirrer. About 99.5% of each sample was titrated using a current of 64.3 ma. The remainder was titrated using a current of 0.643 ma. Amperometric detection of the end-point was employed. A Sargent Model XXI Polarograph was used to measure the current flowing between two silver indicator electrodes at various stages of titration and to apply the potential of 50 mv. between the two electrodes. Before the end-point, the indicator current was limited by the concentration of chloride ion in the solution. After the end-point, it was limited by the concentration of silver ion. Three portions of each of the solutions of separate isotope were titrated. The milliequivalents of chloride ion per gram of solution are given in column 4 of Table I. The $NaCl^{35}$ and $NaCl^{37}$ solutions contained 0.262371 and 0.160266 meq. per gram of solution, respectively. The standard deviation of the individual measurement is estimated to be 0.000071 meq. per gram. However, on examination of a series of solutions containing various concentrations of natural chloride, a concentration dependency was observed. Thus an estimated limit of 3 parts in 10^4 for possible systematic error in the titration data is included in the final statement of the uncertainty component in Table V.

Isotope Analysis of the Separated Isotope Solutions.—The only negative ion observed in the background spectrum of the mass spectrometers was the Cl^- ion. Consequently, considerable effort was made to eliminate any appreciable effect of this background on the accuracy of the measurement

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(10) A. W. Boyd, F. Brown and M. Lounsbury, *Can. J. Phys.*, **33**, 35 (1955).

(11) H. R. Owen and O. A. Schaeffer, *J. Am. Chem. Soc.*, **77**, 898 (1955).

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(14) R. C. Hoering and P. L. Parker, *Geochim. Cosmochim. Acta*, **23**, 186 (1961).

(15) T. J. Murphy, W. S. Clabaugh and R. Gilchrist, *J. Research Natl. Bur. Standards*, **53**, 13 (1954).

Table I

Concentration of Chloride Ion in NaCl^{35} and NaCl^{37} Solutions

Solution no.	Solution wt. (g.)	Chloride ion (meq.)	Concentration (meq./g.)	Deviation from mean
Cl^{35}-A	4.28552	1.124607	0.262420	+0.000049
Cl^{35}-B	4.18748	1.098511	.262332	− .000039
Cl^{35}-C	4.06324	1.066035	.262361	− .000010
		Mean:	.262371[a]	
Cl^{37}-A	5.82249	0.933180	.160272	+ .000006
Cl^{37}-B	5.94181	.951959	.160214	− .000052
Cl^{37}-C	5.72187	.917286	.160312	+ .000046
		Mean:	.160266[a]	

[a] The standard deviation of the individual measurements is estimated to be 0.000071 meq./g. of solution.

of the isotopic composition of the separated isotopes. Starting with AgCl^{35}, a series of measurements were made all using the same set of filaments and filament support. The entire filament assembly was carefully cleaned between each sample loading to hasten the conditioning of these parts of the ion source. The conditioning process was further accelerated during a run by the controlled introduction of hydrogen to a pressure of about 10^{-5} mm. while increasing the temperature of sample and center filaments above that normally used for ratio measurement. Four analyses were made of each isotope with ratios obtained by stepwise increase of ion current until the ratio was independent of further increase in ion current. Then the measurement was continued until the sample was exhausted. At this point, the composition of the background chlorine signal was better than 99% of the composition of the separated isotope under study. Figure 1 shows a plot of the data obtained in this manner for AgCl^{37}. The final isotopic composition is indicated as well as the estimated limits of error. The limits set on the isotopic composition of the separated isotopes include a liberal estimate of possible bias for the upper limit whereas that for the lower limit is simply a confidence-limit statement. The isotopic composition of the separated isotopes used in the preparation of the calibration samples is given in Table II. The respective Cl^{35} and Cl^{37} isotopic compositions as reported by ORNL were "Cl^{35}" 99.56 ± 0.05 atom % Cl^{35}, 0.42 ± 0.05 atom % Cl^{37}; "Cl^{37}" 0.72 ± 0.05 atom % Cl^{35}, 99.28 ± 0.05 atom % Cl^{37}. The ORNL limits quoted are an expression of the precision of the measurement. The error is estimated at less than 1% from known sources of systematic error.

Table II

Isotopic Composition of Purified Chlorine Isotopes Used in Calibration Samples

Isotope	Isotopic composition[a] (atom %)
Cl^{35}	Cl^{35} = 99.600 $^{+0.015}_{-.004}$
	Cl^{37} = 0.400 $^{-.015}_{+.004}$
Cl^{37}	Cl^{35} = 0.735 $^{-.035}_{+.007}$
	Cl^{37} = 99.265 $^{+.035}_{-.007}$

[a] The limits set on the isotopic composition of the separated isotopes include a liberal estimate of possible bias for the upper limit whereas that for the lower limit is simply a confidence-limit statement.

Preparation of the Calibration Samples.—Each isotope solution was thoroughly shaken and the ground glass surfaces of the stopper and flask were wiped dry. The flasks were then weighed with an accuracy of ± 0.02 mg. Aliquots were withdrawn from each flask by pipets in such amounts as to approximate the natural chlorine isotope ratio when mixed and to contain about 25 mg. of total chlorine. The flasks were again weighed to determine the actual amount of solution withdrawn. The aliquots were transferred to a beaker, the pipets were rinsed thoroughly with water and the washings were added to the beaker. The resulting mixture of the two aliquots of isotope solutions was carefully stirred, and a few drops of nitric acid and an excess of silver nitrate solution were added. The precipitated silver chloride was allowed to stand in the dark overnight. The solution was filtered through a fine porosity porcelain filter and the precipitate was washed with distilled water. The silver chloride was taken into solution with 1 ml. of concentrated ammonium hydroxide and drawn through the filter into a small vial. The filter was washed twice with 0.5 ml. portions of ammonium hydroxide. The isotopic composition of each mixture was calculated from the weights of the isotopic solutions mixed, the titration assay of total chlorine in the isotope solutions, and the mass spectrometric analysis of the isotopic composition of the isotope solutions. Each calibration mixture was analysed twice on each instrument with three ratio determinations per analysis. The calculated and observed values were compared to determine the individual instrument bias.

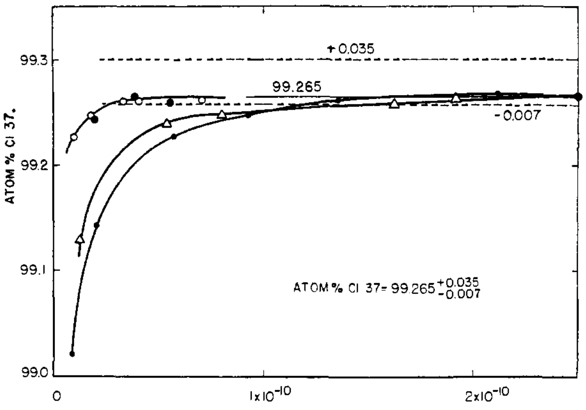

Fig. 1.—Determination of the isotopic composition and limits of error for the Cl^{37} separated isotope solution.

Natural Samples.—The reference chloride material is a commercial sample of sodium chloride stored as NBS Isotope Reference Sample No. 105. The mineral samples are halite or sylvite crystals. Seven samples were obtained from the collections of the U. S. National Museum through the courtesy of Paul E. Desautels, Associate Curator, Division of Mineralogy and Petrology. Small chips were broken from each crystal, dissolved and converted to silver chloride as in the case of the calibration samples.

Results and Discussion

Table III summarizes the isotopic abundance ratio Cl^{35}/C^{37} in five calibration mixtures and as observed with mass spectrometers MS-3 and MS-4. Columns 5 and 6 of the table indicate random fluctuations in a consistent bias for each instrument.

Table III

Calculated and Observed Isotopic Ratios of Chlorine in Calibration Mixtures

	Isotopic ratio, Cl^{35}/Cl^{37}			Bias (calcd./obsd.)	
Mixture	Calcd.	Obsd., MS-3	Obsd., MS-4	MS-3	MS-4
C	3.1598	3.1688	3.1584	0.99716	1.00044
D	3.1509	3.1606	3.1536	.99693	0.99914
F	3.1286	3.1337	3.1258	.99837	1.00090
G	3.0689	3.0719	3.0678	.99902	1.00036
H	3.1116	3.1160	3.1040	.99858	1.00245
			Mean:	.99801	1.00066
			Uncertainties:[a]	+ .0028 − .0030	+0.0028 −0.0030

[a] Over-all limits of error based on 95% confidence limits for the mean and on allowances for the effects of known sources of possible systematic error.

The opposed direction of bias for the two instruments makes difficult any interpretation of the bias except as an over-all correction factor to be applied to the observed isotope abundance ratios.

Table IV summarizes the average ratio of ratios as observed by the two mass spectrometers for the NBS Isotope Reference Sample No. 105 compared with the seven mineral samples. These data are insufficient to justify a statement on the absence of a natural variation in isotope abundance to less than 0.2% of the Cl^{35}/Cl^{37} ratio. However, the work of Hoering and Parker[14] on a comparison of NBS Isotope Reference Sample No. 105 with 81 samples of natural occurrence from widely scattered localities shows no variation beyond their stated limits of 0.1% of the ratio. Consequently, the observed abundance ratio for Reference Sample No. 105 is taken as representative of natural chlorine. To obtain the absolute abundance ratio, however, the observed ratio must be corrected for the average bias of the appropriate instrument. Thus for MS-3, the corrected Cl^{35}/Cl^{37} ratio for the reference sample is (3.1327)(0.99801) = 3.1265 and for MS-4, the corrected ratio is (3.1258)(1.00066) = 3.1279. The average, $3.1272\,^{+0.0079}_{-0.0082}$ is taken to be the absolute abundance ratio and results in the percentage abundances $Cl^{35} = 75.770_5\,^{+0.044}_{-0.046}$ and $Cl^{37} = 24.229_5\,^{-0.044}_{+0.046}$.

TABLE IV

ISOTOPIC ABUNDANCE RATIOS OF CHLORINE FROM VARIOUS SOURCES RELATIVE TO NBS ISOTOPE REFERENCE NO. 105

Sample[a]	Description	Average observed ratio of ratios[b]
64736	Halite, Stassfurt, Germany	1.0005
46249	Halite, Petit Ansee, Louisiana	1.0003
24989	Halite, Mormon Mine, St. Thomas District, Lincoln Co., Nevada	0.9997
73500	Halite, Cumana, Venezuela	0.9989
8074	Halite with Sylvite, Kalusz, Galicia, Poland	1.0011
103518	Sylvite, Georg Unstrut Potash Shaft, Nebra, Germany	1.0006
104752	Sylvite, U. S. Potash Co. Mine, Carlsbad, N. M.	1.0002

[a] U.S. National Museum Catalog Numbers. [b] $[Cl^{35}/Cl^{37}]_{Ref.}$ $[Cl^{35}/Cl^{37}]$ Mineral. The 95% confidence limit is ± 0.0020.

Everling, König, Mattauch and Wapstra[16] have tabulated a complete and consistent list of relative nuclidic masses computed by means of least squares methods from all significant experimental data available to them. On the unified mass scale ($C^{12} = 12$), they report $Cl^{35} = 34.9688545 \pm 0.0000028$ and $Cl^{37} = 36.9658959 \pm 0.0000022$. The uncertainties are the standard error determined by internal consistency. Combining the percentage abundance of the isotopes and the nuclidic masses results in an atomic weight on the unified scale ($C^{12} = 12$) of $35.45273\,^{+0.00092}_{-0.00097}$. Using the factor 1.000317917[16] to convert from the unified scale to the physical scale ($O^{16} = 16$) and then the factor 1.000275 to convert from the physical to the chemical scale (O = 16) results in the values 35.46400 ($O^{16} = 16$) and 35.45425 (O = 16), respectively. These calculations are summarized in Table V. The latter value is significantly different from that reported by the I.C.A.W. at the 1957 meeting.[3] However, the above chlorine atomic weight, 35.45273 ($C^{12} = 12$) compared with the silver atomic weight reported by Shields, Craig and Dibeler[1,2] gives a combining weight ratio Cl/Ag = 0.328667_1 in excellent agreement both with the original work of Richards and Wells[5] and the pooled chemical combining weight data.[6] The satisfactory consistency supports the precise chemical determination of the combining weight ratio (although not the chemical determination of the atomic weights) and the mass spectrometric determination of the atomic weight of silver.

TABLE V

SUMMARY CALCULATION OF THE ATOMIC WEIGHT OF CHLORINE[a]

Corrected isotopic ratio:	$Cl^{35}/Cl^{37} = 3.1272\,^{+0.0079}_{-\ .0082}$
Corrected isotopic composition, Atom %	$Cl^{35} = 75.770_5\,^{+0.044}_{-\ .046}$ $Cl^{37} = 24.229_5\,^{-\ .044}_{+\ .046}$
Nuclidic masses ($C^{12} = 12$)[b]	$Cl^{35} = 34.9688545 \pm 0.0000028$ $Cl^{37} = 36.9658959 \pm 0.0000022$
Unified atomic weight ($C^{12} = 12$)	$= 35.45273\,^{+0.00092}_{-0.00097}$
Uncertainty components:	
Ratio determination	$= \pm 0.00039_7$ (Random error)
Composition of separated isotopes	$= ^{+\ .00021}_{-\ .00026}$ (Limit of systematic error)
Titration of separated isotope solutions	= ± .00031 (L.S.E.)
Nuclidic masses	$= \pm .00000_3$ (L.S.E.)
Total	$= ^{+\ .00092}_{-\ .00097}$

Conversion factor ($C^{12} = 12$) to ($O^{16} = 16$) scale = 1.000317917[b]
Physical atomic weight ($O^{16} = 16$) = 35.46400
Conversion factor ($O^{16} = 16$) to (O = 16) scale = 1.000275[c]
Chemical atomic weight (O = 16) = 35.45425

[a] Except as otherwise indicated, the uncertainties are over-all limits of error based on 95% confidence limits for the mean and allowances for effects of known sources of possible systematic error. [b] See ref. 16. [c] See ref. 1.

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