The Isotopic Constitution of Calcium, Titanium, Sulphur and Argon

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A mass-spectrographic study of the isotopic constitution of calcium, titanium, and sulphur has been made. Two new calcium isotopes, Ca^{46} and Ca^{48}, were found, present with abundances 1/29,000 and 1/520 that of Ca^{40}, respectively. No new titanium isotopes were found. A new sulphur isotope, S^{36}, was discovered, having an abundance 1/6,000 that of S^{32}. The proof for the existence of the new isotopes is presented. The relative abundances of the isotopes in these three elements were determined. A search for other possible rare isotopes was made in all mass number positions in the immediate neighborhood of the known isotopes. Upper limits for the existence of these hypothetical isotopes are given. A search was made for A^{42}.

THIS paper is one of a series dealing with the study of the isotopic constitution of the elements. A systematic research program was undertaken with the following objectives in mind: (1) To obtain accurate measurements of the relative abundances of isotopes (2) to establish the existence or nonexistence of questionable isotopes, and (3) to search in all mass number positions in the immediate neighborhood of the known isotopes for possible rare isotopes, and if none was found, to set upper limits for the existence of such hypothetical stable isotopes.

The elements which so far have been studied are A, K, Rb, Zn, and Cd;[1] Hg, Xe, Kr, Be, I, As, and Cs;[2] and Os.[3] A preliminary report has been given for Pb.[4] The present paper will show the results obtained for calcium, titanium and sulphur, together with an additional result for argon.

Apparatus

The mass spectrometer used differed from that employed for the Hg, Xe, etc., study only insofar as a new tube was employed which enabled one to work with substances not volatile at ordinary temperatures. In the earlier work it was necessary that the substance to be studied should have a vapor pressure at least as great as 10^{-5} mm Hg at the temperature to which it is safe to heat the entire Pyrex tube. The new tube has a small furnace inside of it which now contains the substance to be studied. This small furnace may be heated to any desired temperature.

A diagram of a portion of the new tube is shown in Fig. 1. Its operation is quite similar to that of the previous tube. A ribbon of electrons, the cross section of which is indicated by the dashes between plates J and B, moves perpendicular to the figure. The small furnace G consists of a solid block of Nichrome V 6 mm $\times$6 mm$\times$10 mm long, heated by a one-half mm diameter tungsten spiral filament passing through the upper hole in the block. The substance to be studied is placed in the lower hole, which is closed at one end and has a threaded cap at the other. When the furnace is heated, molecules emerge through the slit below the lower hole and pass into the electron beam. Here positive ions are formed which are drawn through slits S_1 and S_2 into the 180° magnetic analyzer H. This molecular beam method of producing ions was employed with considerable success by Bleakney, Blewitt, Sherr and Smoluchowski[5] in their study of beryllium.

If one varies the energy of the ions and plots a curve of positive ion current collected beyond the exit slit of the analyzer, one obtains a mass spectrum having a peak for each isotope present. The magnetic field is, of course, held constant.

In the present apparatus one is limited to a furnace temperature of about 1200°C. In order to reach higher temperatures a furnace of tantalum will be employed.

Results

Calcium

Calcium metal was placed in the furnace and the entire apparatus was baked out at a tem-

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[1] Nier, Phys. Rev. **50**, 1041 (1936).
[2] Nier, Phys. Rev. **52**, 933 (1937).
[3] Nier, Phys. Rev. **52**, 885 (1937).
[4] Nier, Phys. Rev. **51**, 1007 (1937).

[5] Bleakney, Blewitt, Sherr and Smoluchowski, Phys. Rev. **50**, 545 (1936).

perature of 450°C until only small traces of impurities remained. For the study of calcium a furnace temperature of about 550°C gave positive ion peaks of sufficient magnitude without too great a rate of evaporation from the furnace. A typical mass spectrum is shown in Fig. 2. One sees here, in addition to the previously known isotopes, 40, 42, 43, and 44,[6] two new peaks, one at mass 48 and one at mass 46. That these newly found peaks really correspond to rare isotopes of calcium, and not to possible impurities present, may be concluded from the following:

(1) The abundance ratios Ca^{48}/Ca^{40} and Ca^{46}/Ca^{40} were studied as a function of furnace temperature, i.e., Ca vapor pressure, and were both found to remain constant within the experi-

FIG. 2. Mass spectrum showing isotopes of calcium. Positive ion current expressed in terms of cm deflection of galvanometer at its highest sensitivity. One cm represents about 2.5×10^{-15} ampere.

mental errors. The Ca^{48}/Ca^{40} ratio was studied over a 12-fold range and the Ca^{46}/Ca^{40} ratio over an 8-fold range of pressure.

(2) The results of a study of the number of ions of each isotope formed as a function of the energy of the electrons producing the ions is shown in Fig. 3. From this curve, one sees that not only do the three peaks, Ca^{40}, the peak at 46, and the peak at 48, all have the same form of efficiency curve, but they also have *the same appearance potential*. A detailed study of the form of the curves near the appearance potential showed that the appearance potential of the 48 peak was within at least 0.3 volts of that for Ca^{40}, while that for the 46 peak did not differ more than a volt from that for Ca^{40}.

(3) A study of the doubly charged ions showed that the 24 peak $(48)^{2+}$ had the same form of efficiency curve as did the $(Ca^{40})^{2+}$ peak. The appearance potentials were the same within the experimental error, two volts. The relative height of the two peaks agreed within a few percent of that found for the singly charged ions.

It should be mentioned that a trace of magnesium was present in the calcium. Mg^{24} contributed only about 10 percent of the total 24 peak at 70 volts, the point where the Ca^{2+} current versus electron energy curve has its maximum. As Mg has a much lower appearance potential than Ca^{2+}, and as its efficiency curve is
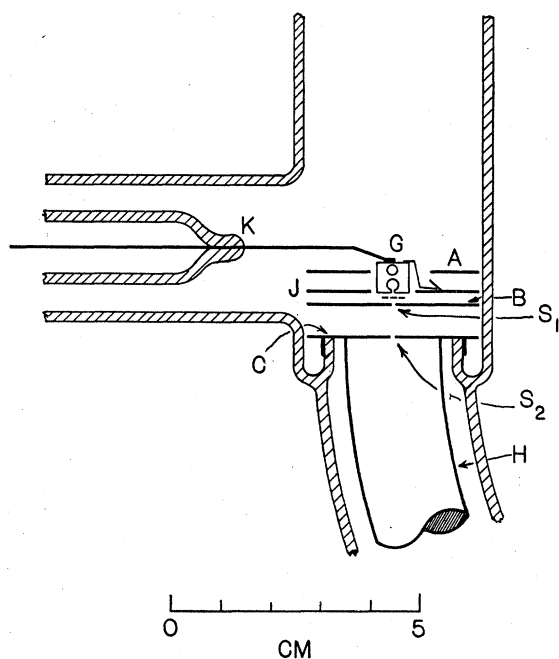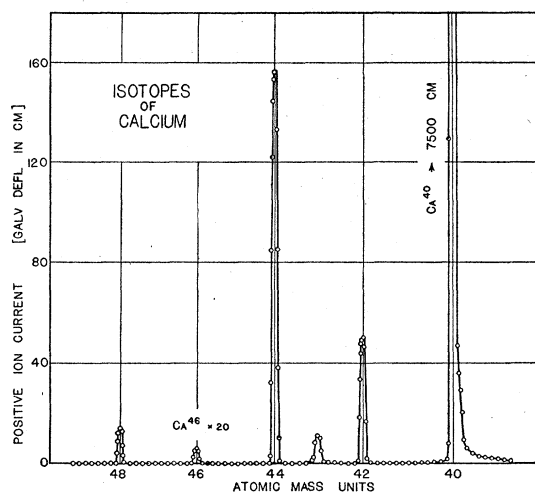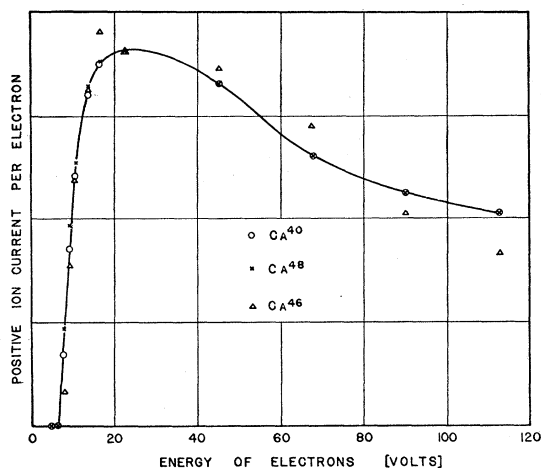

FIG. 1. Diagram of portion of mass spectrometer where ions are produced. The furnace G is supported by the glass stem K. Actually 4 electrical leads come through this stem. Two furnish the current to the furnace filament, one supports the furnace (this is the one shown in the diagram), and the fourth, together with the one supporting the furnace form a thermocouple junction for measuring the furnace temperature. If one cracks the reentry seal of which the stem K is a part, the stem and furnace may be removed without disturbing the rest of the apparatus. The function of the plate A is to support an electron gun and trap which are not shown in the figure. As in the earlier work no wax or grease joints are employed at any point in the apparatus. The entire tube may be thoroughly baked to remove impurities.

[6] Aston, Proc. Roy. Soc. A149, 396 (1935).

FIG. 3. Efficiency of ionization curve for Ca$^+$.

relatively flat for electron energies over the range where Ca^{2+} is formed, no difficulty was had in subtracting the Mg^{24} contribution from the total peak, and thus arriving at the conclusions of the previous paragraph.

It was not possible to examine the (Ca^{46})$^{2+}$ due to the fact that it was small as compared with a trace of sodium present in the calcium. The discovery of Ca^{46} confirms the result of Wigner,[7] who computed that Ca^{46} should be stable.

Table I shows a list of the stable isotopes of Ca, together with their respective abundances. Aston's values, converted from percentages to relative abundances, are also included.

All of the measured abundances, with the exception of that for Ca^{46}, are believed to be correct to 3 percent. The abundance for Ca^{46} may be in error by 15 percent. However, we have not taken account of the possible effect of free evaporation from the furnace. The mass of the heaviest Ca isotope differs by 20 percent from that of the lightest; only in hydrogen do the isotopes have a larger fractional spread in mass. In the case of *ideal* distillation of Ca from the furnace, the Ca^{48}/Ca^{40} ratio *as measured* would be only $(40/48)^{\frac{1}{2}}=0.895$ of what it should be. The other isotope ratios as measured would be in error by similar factors.

As the calcium atoms are evaporated from a solid surface and not from a liquid where mixing can take place, it does not seem likely that one

[7] Wigner, Phys. Rev. 51, 947 (1937).

would approach the ideal case. However, the effect should not be overlooked in this work.

The major problem of the present study of calcium was the establishment of the existence or nonexistence of rare isotopes. The relative abundances of the Ca isotopes will be examined in greater detail later.

With a packing fraction of -6 and a conversion factor of 1.000275 for going from the atomic to the chemical scale, one computes a chemical weight of 40.08 from both the writer's and Aston's values. The present chemical value is 40.08.

A search for other isotopes was also made. None was found, and it was possible to set the following upper limits for the abundances relative to Ca^{40}: Ca^{38}, 1/60,000; Ca^{39}, 1/40,000; Ca^{41}, 1/150,000; Ca^{45}, Ca^{47}, Ca^{49}, and Ca^{50}, 1/200,000. Aston had set an upper limit of 1/1000 for Ca^{41}.

Titanium

Titanium fluoride, TiF$_3$, was introduced into the furnace. It was found that the molecular ions were the most convenient to examine. A typical mass spectrum is shown in Fig. 4. The isotopes found were the same as those reported by Aston.[6]

Table II gives a list of the isotopes, together with their respective abundances. Aston's values are included for comparison. With a packing fraction of -7.2[8] and a conversion factor of 1.000275, the writer's values give a chemical weight of 47.88. Aston's figures yield the value 47.90. The present chemical value is 47.90. The writer believes that his abundances relative to Ti^{48} are all correct to 2 percent. The effect of free evaporation should be negligible here, as the spread in mass units between the heaviest and lightest ions is only 4 at mass 105.

The real reason for undertaking the study of

TABLE I. *Isotopes of calcium.*

	MASS NUMBER					
	40	42	43	44	46	48
Abundance	100	0.66	0.150	2.13	0.0034	0.191
Aston's values	100	0.80	0.18	2.35	—	—

[8] Dempster, Bull. Am. Phys. Soc., Chicago Meeting, November, 1937.

titanium was to see if any other isotopes existed. None was found, and it was possible to set the following upper limits of abundance relative to Ti^{48}: Ti^{42}, 1/100,000; Ti^{43}, 1/10,000; Ti^{44} and Ti^{45}, 1/50,000; Ti^{51}, Ti^{52}, and Ti^{53}, 1/100,000; Ti^{54}, 1/25,000. Some difficulty with impurities was encountered in this search. However, it was possible to suppress the impurities in the several positions where they occurred below the limits given above.

Sulphur

Aston[9] found sulphur to consist of three isotopes, 32, 33, and 34, present in abundances roughly proportional to the numbers 96, 1, and 3, respectively. The present work on sulphur was undertaken in order to search for a possible S^{36} isotope, which Wigner[7] calculated should be stable.

After thoroughly outgassing the apparatus, SO_2 was allowed to flow into the tube through a capillary leak, the pressure being maintained below 10^{-4} mm mercury. No use was made of the small furnace in this case. Table III tabulates all of the ions observed in the SO_2^+, SO^+ and S^+ spectra and possible combinations of sulphur and oxygen isotopes which would produce ions of these masses. Combinations such as $SO^{17}O^{17}$ and $SO^{17}O^{18}$, which are very rare, are not included in the table.

Before proceeding to the proof that S^{36} exists it will be well to establish the abundances of the other sulphur isotopes. The relative abundances of S^{32}, S^{33}, and S^{34} were determined from the relative heights of the 64, 65, and 66 peaks in the SO_2^+ spectrum, and from the relative heights of the 48, 49, and 50 peaks in the SO^+ spectrum. As may be seen from the table, allowance has to be made for the rare oxygen isotope combinations in determining these abundances. Throughout this paper the isotopes of oxygen

TABLE II. *Isotopes of titanium.*

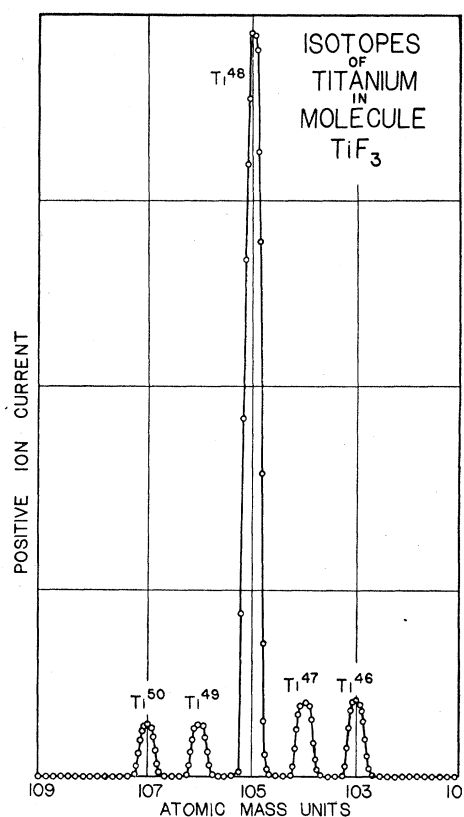|	MASS NUMBER				
	46	47	48	49	50
Abundance	10.82	10.56	100	7.50	7.27
Aston's values	11.9	10.9	100	7.7	9.7

[9] Aston, *Mass Spectra and Isotopes*, p. 143.

FIG. 4. Mass spectrum showing isotopes of titanium.

and their abundances are assumed to be: O^{16}, 100; O^{17}, 0.04; and O^{18}, 0.20. The results obtained for sulphur are then S^{32}, 100; S^{33}, 0.78; and S^{34}, 4.4. The values given are believed correct to two percent. It should be mentioned that these results are not greatly influenced by the exact abundances assumed for the oxygen isotopes.

That S^{36} exists may be concluded from the following:

(1) From a consideration of the relative heights of the 68 and the 64 peaks we find that only approximately one-half of the 68 peak can be attributed to the ions $(S^{34}O^{18}O^{16})^+$ and $(S^{32}O^{18}O^{18})^+$. We are thus forced to conclude that the remainder is due either to an impurity or to S^{36} in the ion $(S^{36}O^{16}O^{16})^+$ present to one part in 6000 ± 10 percent, compared with S^{32}. The excellent agreement between the efficiency curves shown in Fig. 5A makes the impurity possibility unlikely.

(2) From a comparison of the relative heights of the 52 and 48 peaks in the SO^+ spectrum we

find that only about $\frac{1}{3}$ of the height of the 52 peak can be attributed to $(S^{34}O^{18})^+$. The residue must thus again be due either to an impurity or to S^{36} in $(S^{36}O^{16})^+$. If one assumes the latter possibility, *the S^{36}/S^{32} ratio again turns out to be $1/6000\pm10$ percent.* The excellent agreement between the efficiency curves shown in Fig. 5B also makes the impurity hypothesis unlikely.

(3) The relative heights of the 36 and 32 peaks are *also in the ratio $1/6000\pm10$ percent.* Fig. 5C shows the efficiency curves for these two peaks, which also agree remarkably well when one considers the low probability of this ionization process.

The 67 peak observed in SO_2^+ was shown from a measurement of its abundance to be due entirely to $(S^{34}O^{17}O^{16})^+$ and $(S^{33}O^{18}O^{16})^+$. The 51 peak in SO^+ was found to be due entirely to $(S^{34}O^{17})^+$ and $(S^{33}O^{18})^+$. No peak was observed at mass 35 in the S^+ spectrum. In *each* of these three positions we are able to set an upper limit of $1/50,000$ for the abundance of S^{35}.

A study of the other mass number positions enables us to set the following upper limits for the abundance of other possible isotopes relative to S^{32}: S^{37} and S^{38}, $1/200,000$; S^{31}, $1/20,000$; S^{30} $1/50,000$.

With a packing fraction of -5.6 for sulphur and a conversion factor of 1.000275 in going from the atomic to the chemical scale, an atomic weight of 32.064 is computed for sulphur. The present chemical value is 32.06.

Argon

In the earlier work on argon[1] an upper limit of $1/20,000$ of A^{40} was set for A^{42}. After discovering the new calcium and sulphur isotopes at this
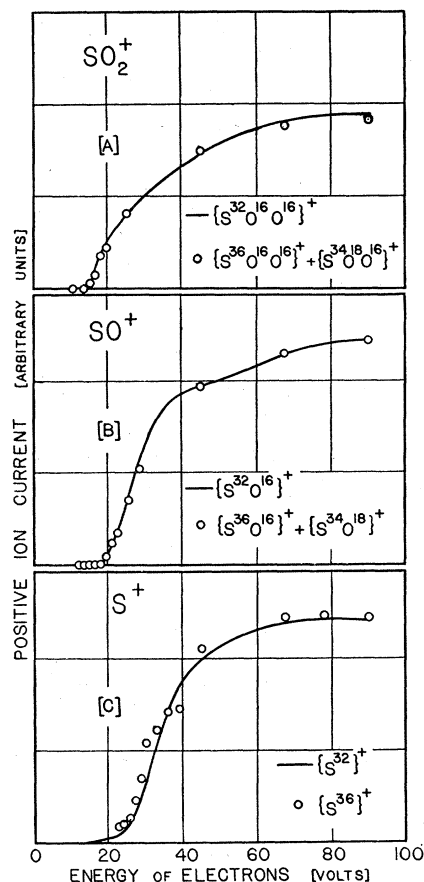
TABLE III. *Ions observed from SO_2.*

TYPE OF ION	MASS NUMBER	POSSIBLE COMBINATIONS PRODUCING IONS AT THESE MASS NUMBERS
SO_2^+	64	$(S^{32}O^{16}O^{16})^+$
	65	$(S^{33}O^{16}O^{16})^+$, $(S^{32}O^{17}O^{16})^+$
	66	$(S^{34}O^{16}O^{16})^+$, $(S^{32}O^{18}O^{16})^+$, $(S^{33}O^{17}O^{16})^+$
	67	$(S^{34}O^{17}O^{16})^+$, $(S^{33}O^{18}O^{16})^+$, possibly $(S^{35}O^{16}O^{16})^+$
	68	$(S^{36}O^{16}O^{16})^+$, $(S^{34}O^{18}O^{16})^+$, $(S^{32}O^{18}O^{18})^+$
SO^+	48	$(S^{32}O^{16})^+$
	49	$(S^{33}O^{16})^+$, $(S^{32}O^{17})^+$
	50	$(S^{34}O^{16})^+$, $(S^{32}O^{18})^+$, $(S^{33}O^{17})^+$
	51	$(S^{34}O^{17})^+$, $(S^{33}O^{18})^+$, possibly $(S^{35}O^{16})^+$
	52	$(S^{36}O^{16})^+$, $(S^{34}O^{18})^+$
S^+	32	$(S^{32})^+$
	33	$(S^{33})^+$
	34	$(S^{34})^+$
	36	$(S^{36})^+$

FIG. 5. Efficiency of ionization curves for SO_2^+, SO^+, S^+. The ion $(S^{32}O^{18}O^{18})^+$ is not listed in part A as a contribution to the 68 peak. It is quite negligible, contributing only approximately 1 percent to the peak. The curves in the three parts of the figure are the ones for the most abundant sulphur isotope, S^{32}. In order to avoid confusion the experimental points are not shown. The circles are the experimental points for the ions involving the isotope S^{36}. It is hardly necessary to state that there is a large scale factor between the data involving S^{36} and that involving S^{32}.

time it seemed worth while to look further for A^{42}. It is now possible to say that if it exists it must be less than $1/300,000$ of A^{40}.