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Isotopic Composition of Sulphur from ZnS, FeS₂ and PbS Ores ***

Skład izotopowy siarki z rud ZnS, FeS₂ i PbS

Изотопный состав серы из руд ZnS, FeS₂ и PbS

CHEMICAL PREPARATION OF SAMPLES

The isotopic abundance ratios of sulphur were determined using sulphur dioxide which was introduced into the spectrometer in gaseous state. Therefore, the samples of ZnS, FeS₂ and PbS were oxidized in oxygen atmosphere in a specially designed glass apparatus shown in Fig. 1. It is composed of a quartz tube C, in which the sulphides are oxidized, a spiral D in which the sulphur dioxide is condensed, and of appropriate taps and ground joints.

Oxygen from a steel bottle is passed through a washer into the quartz tube C. The sample is introduced in a quartz vessel C₁. As the sample must be heated to 500—1 000°C, the tube C is closed by the water-cooled ground glass joints B and B₁.

The resulting sulphur dioxide is desiccated over P₂O₅ in the vessel A₁ and enters the spiral D immersed in a Dewar flask filled with solid carbon dioxide where the gas is condensed.

After the sample is completely oxidized and the sulphur dioxide liquefied in the spiral, the tap K₂ is closed, the taps K₃ and K₅ opened, a vessel for SO₂ connected to the ground joint K₁ and the whole system evacuated. The tap K₅ is then closed and spiral D removed from the

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Dewar flask. As the temperature rises, the sulphur dioxide evaporates filling the vessel connected to K_1 . When the pressure inside the apparatus reaches 760 mm Hg the evaporation is stopped by cooling the spiral D again.

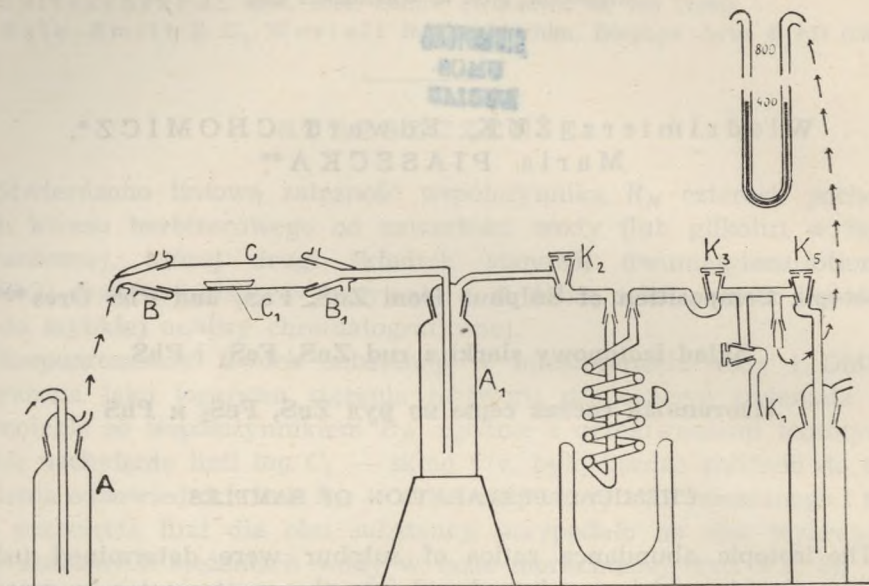


Fig. 1. The apparatus for samples preparation of SO_2

The apparatus permitted to prepare SO_2 from ZnS and FeS_2 quite easily, and nearly total sulphur was oxidized to SO_2 . The preparation of SO_2 from PbS occurred only when the temperature of the glass tube was increased to $1\ 000^\circ\text{C}$. The oxidation process was slower and the yield much lower due to some remains of unoxidized sample on the walls of tube C. Under conditions of increased temperature both the vessel C_1 and the tube C were destroyed quite rapidly.

When a new sample was to be investigated, the apparatus was cleaned in order to avoid any contamination by the remains of the previous samples.

METHOD OF DETERMINATION

The measurements of the isotope composition of sulphur were carried out using a mass spectrometer with a 60° magnetic field with a single collector; the ionic currents were measured employing a well-standardized vibrational electrometer. The 66 and 64 peaks of the

mass spectra were obtained by changing the magnetic field within the necessary interval. The spectra were recorded on a recorder.

Only the isotopic composition of ZnS was determined in a series of absolute measurements; the measurements of isotopic composition of sulphur from FeS₂ and PbS were corrected relatively to the sulphur isotope results from ZnS. In order to make the relative determinations possible, the source of gas was composed of two containers, from which the gas could be alternately introduced into the spectrometer (Fig. 2).

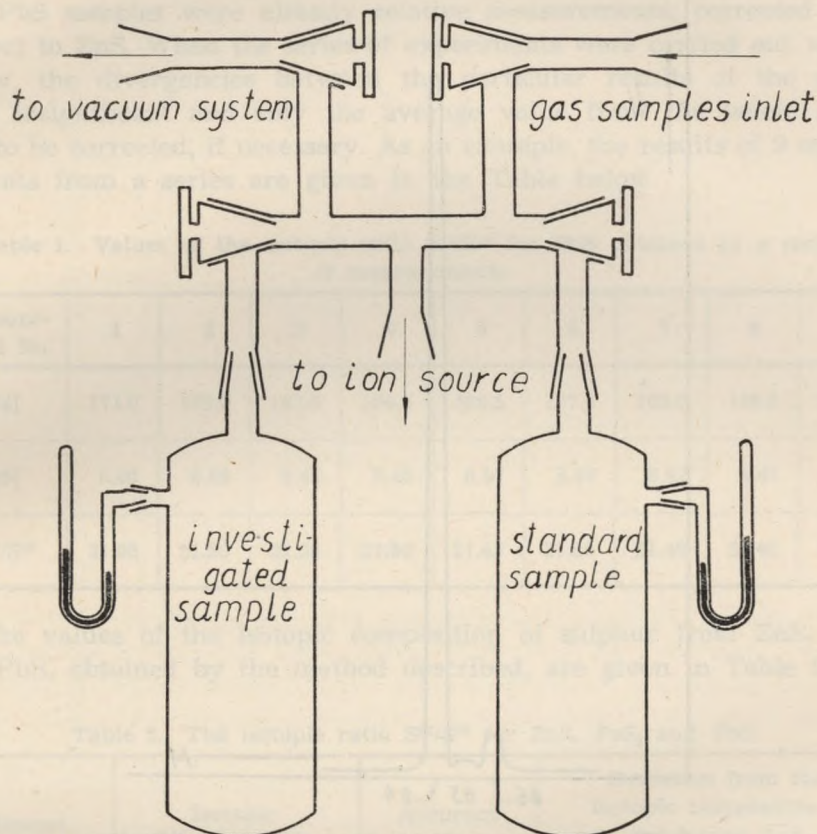


Fig. 2. The double container system for gas samples inlet into the ion source of the mass spectrometer

One of the containers was filled with SO₂ from the reference samples, the other contained SO₂ from the sample investigated. The isotopic composition of the reference sample was determined, both before and after a series of measurements, so that appropriate corrections could be made.

THE ISOTOPIC COMPOSITION OF SULPHUR

The mass spectrum of sulphur dioxide has peaks, [66] and [64]; by measuring the peak heights, the isotopic abundance ratio S^{32}/S^{34} can be calculated. The peak [66] is due to three ion species, $S^{34}O_2^{16+}$, $S^{32}O^{16}O^{18+}$ and $S^{33}O^{16}O^{17+}$, the contribution from the third ion being insignificant. On the other hand, the peak [64] is due to $S^{32}O_2^{16+}$ ions and its height is more than 21 that of the [66] peak.

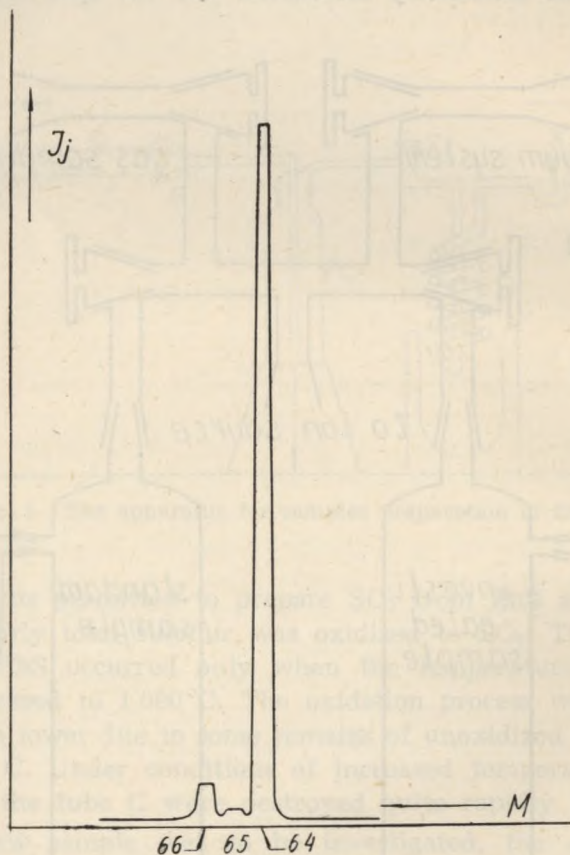


Fig 3. The SO_2 mass spectrum by constant amplification

From the ratio of peak [66]/[64] the ratio of the abundances of S^{32} and S^{34} isotopes in the element can be calculated directly from the formula:

$$S_{32}/S_{34} = \frac{1}{\frac{[66]}{[64]} - 2 \frac{0_{18}}{0_{16}}} = \frac{1}{\frac{[66]}{[64]} - 0.004}$$

In the above formula O^{18}/O^{16} denotes the isotope ratio of oxygen, the normal isotopic composition of oxygen being 0.002.

The isotopic composition of sulphur for SO₂ obtained from ZnS was determined on the basis of more than 50 measurements carried out over a long period of time and for SO₂ gas prepared from the same standard sample also in various periods of time. From these determinations, the mean value of the isotopic ratio S^{32}/S^{34} for the sample investigated was found to be 21.39 ± 0.02 .

The determinations of the isotopic composition of sulphur for FeS₂ and PbS samples were already relative measurements, corrected with respect to ZnS. When the series of experiments were carried out within a day, the divergencies between the particular results of the series were insignificant and only the average value from the whole series had to be corrected, if necessary. As an example, the results of 9 measurements from a series are given in the Table below.

Table 1. Values of the isotopic ratio S^{32}/S^{34} for PbS obtained in a series of measurements

Measurement No	1	2	3	4	5	6	7	8	9
[64]	171.0	168.0	167.0	166.5	166.5	167.0	165.0	166.0	165.5
[66]	8.65	8.55	8.45	8.45	8.47	8.47	8.42	8.47	8.43
S^{32}/S^{34}	21.55	21.50	21.55	21.50	21.45	21.50	21.40	21.40	21.45

The values of the isotopic composition of sulphur from ZnS, FeS₂ and PbS, obtained by the method described, are given in Table 2.

Table 2. The isotopic ratio S^{32}/S^{34} for ZnS, FeS₂ and PbS

Mineral	Isotopic ratio S^{32}/S^{34}	Accuracy %	Deviation from the isotopic composition of sulphur in ZnS	
			Absolute value	%
ZnS	21.39 ± 0.02	0.1	0	0
FeS ₂	21.75 ± 0.04	0.2	0.36	1.7
PbS	21.47 ± 0.02	0.1	0.08	0.4

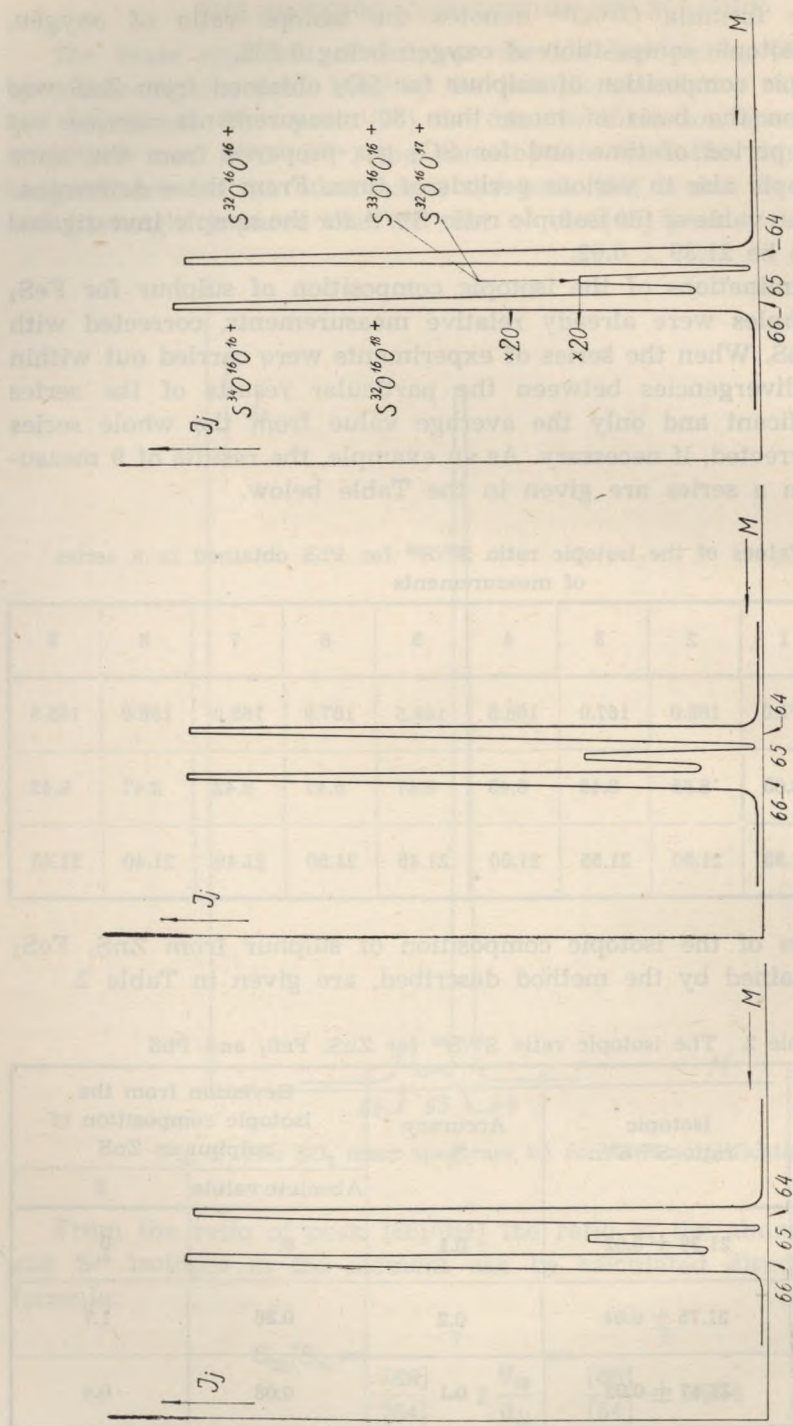


Fig. 4. The examples of SO_2 mass spectrum obtained from; a — ZnS, b — FeS_2 , c — PbS

The above obtained variations in the isotope abundances of sulphur depend on the compound from which sulphur in the form of sulphur dioxide was obtained. The divergencies of the S³²/S³⁴ ratios markedly exceed the possible error of the method of determination of the isotope composition. Other authors report that the effect of fractionation of isotopes which may occur during chemical preparation of SO₂ does not exceed 0.05 and is also much smaller than the variations in the isotope composition obtained in this work for various compounds of sulphur.

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STRESZCZENIE

Używając spektrometru mas przeprowadzono badania składu izotopowego siarki z pokładów ZnS, FeS₂ i PbS Kopalni „Bolesław” w Bolesławiu k. Olkusza. Próbkę ZnS i PbS wydobyto z głębokości ok. 42 m. Pochodziły one z warstw dolomitów kruszczońskich należących do środkowego triasu. Badana próbka piryty wydobyta została z głębokości 50 m z pokładów dolnego triasu.

Siarczki utleniano i dla uzyskanego dwutlenku siarki wyznaczano stosunki wysokości wierzchołków o liczbach masowych 66/64, co pozwalało następnie na określenie stosunku izotopu siarki S³²/S³⁴ w próbce. W serii pomiarów bezwzględnych wyznaczano stosunek izotopów siarki 32/34 w próbce ZnS jako równy 21.39 ± 0.02 . Próbkę tę przyjęto jako wzorcową i na podstawie pomiarów względnych określono skład izotopowy siarki dla próbki FeS₂ jako równy 21.75 ± 0.04 oraz PbS jako równy 21.47 ± 0.02 .

РЕЗЮМЕ

С помощью масс-спектрометра исследовался изотопный состав серы происходящей из месторождений ZnS, FeS₂ и PbS рудника „Болеслав” в Болеславе близ Олькуша. Образцы ZnS и PbS получены из глубины около 42 м, они происходят из средне триасовых пород доломитов содержащих руду. Образец пирита получен из нижне триасовых залежей находящихся на глубине 50 м.

Сульфиды окислялись и для полученной нами двуокиси серы было измерено отношение пиков соответствующих массовым числам 66/64, что в следующем давало возможность найти отношение изотопов серы S³²/S³⁴ в образце. В результате серии абсолютных измерений нами установлено что отношение изотопов S³²/S³⁴ в образце ZnS равно 21,39 ± 0,02. Образец считался стандартным и из относительных измерений найден изотопный состав серы в FeS₂ равный 21,75 ± 0,04 а также в PbS равный 21,47 ± 0,02.

STRESZCZENIE

Używając spektrometru mas przeprowadzono badania izotopowego składu siarki w kruszence z pokładów ZnS, FeS₂ i PbS kopalni „Bolesław” w Bolesławie k. Orlowa. Próbkę ZnS i PbS wydobyto z głębokości ok. 42 m, pochodzą one z warstw dołomitów kruszonośnych należących do średnio-triasowych łazew zawierających rudę. Próbkę pirytu wydobyto z głębokości 50 m z pokładów dolnego triasu.

Szacunki określono i dla uzyskanego dwutlenku siarki wyznaczono stosunek wysokości wierzchołków o liczbach masowych 66/64 do całkowitej wysokości szczytu izotopu siarki S³² w próbce. W wyniku serii pomiarów ustalono, że stosunek izotopów siarki S³²/S³⁴ w próbce ZnS jest równy 21,39 ± 0,02. Próbkę uważano za standardową i z pomiarów względnych ustalono, że stosunek izotopów siarki S³²/S³⁴ w próbce FeS₂ jest równy 21,75 ± 0,04, a także w próbce PbS jest równy 21,47 ± 0,02.