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A Simple Method for the Determination of Sulfide- and Sulfate-Sulfur in Geological Materials by Using Different Temperatures of Decomposition

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Einfaches Verfahren zur Bestimmung von Sulfid- und Sulfatschwefel in geologischen Proben unter Ausnutzung unterschiedlicher Zersetzungstemperaturen

Key words: Best. von Sulfid, Sulfat in Geolog. Material; Zersetzungstemperatur

The determination of the sulfide- and sulfate-sulfur contents of geological samples may be a useful tool for solving geochemical problems. In a previous paper [7] a simple and rapid method for the determination of total sulfur in samples from different origins is described. There it was also mentioned that perhaps sulfide and sulfate species could be distinguished by their different temperatures of decomposition in an oxygen atmosphere. Here I want to present some further experimental results which support the possibility of using the different temperatures of decomposition of certain naturally occurring sulfides and sulfates in determining their amount.

The experiments were carried out by coulometric titration following combustion in an oxygen atmosphere at different temperatures. For more detailed information on the apparatus and procedure the reader is referred to Lange and Brumsack [7].

Pyrite and gypsum (anhydrite) are by far the most abundant sulfur-minerals in the geological environment, if metal deposits are not concerned. Pyrite is also the most stable of the more abundant sulfide-minerals. Gypsum (anhydrite) by contrast decomposes already at relatively low temperatures, whereas the second most abundant sulfate-mineral, barite, is very stable.

For these reasons it was tested, whether pyrite and gypsum could be distinguished (1) as pure substances, (2) in mixtures, and (3) in mixtures with clay as matrix.

Figure 1 shows the results of these experiments. Pure pyrite is decomposed completely at temperatures of less than 700°C, whereas gypsum (anhydrite) starts to release sulfur at temperatures of more than 900°C. In a second experiment a mixture of pyrite and gypsum (with the sulfur being 50% sulfide and sulfate) was continuously heated and the amount of sulfur released determined. It can be seen that, again, pyrite is completely decomposed at the temperature gypsum starts releasing sulfur. In the third experiment a mixture of 1% sulfur (0.5% sulfide and sulfate) was prepared in sulfur-free clay (brick with less than 0.02% sulfur) and treated in the same way as the other samples. Again, Fig. 1 shows a distinct minimum in sulfur-release in the temperature range from 650–800°C.

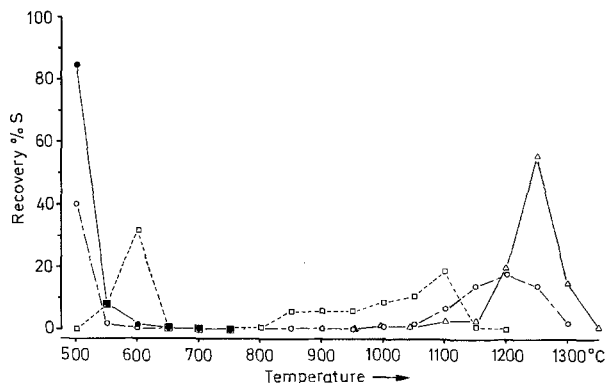


Fig. 1. Decomposition temperatures. ●—● pyrite; △—△ gypsum (anhydrite); ○—○ mixture of pyrite and gypsum; □—□ mixture of 1% sulfur (as pyrite and gypsum) in clay

Table 1

Reference	$\delta^{34}\text{S}^*$
Anger [1]	+26.5 to +30.3 (barite)
This work	+29.5 (sulfate-sulfur, > 1300°C)
Anger [1]	+13.5 (mixed sulfide)
This work	+13.8 (sulfide-sulfur, < 700°C)

* In ‰ relative to the Canyon Diabolo meteorite standard

Unfortunately, a standard reference material for sulfide- and sulfate-sulfur does not exist. For this reason a well examined ore-sample from the “Rammelsberg” ore-deposit in the “Harz” mountains (West-Germany) (“Liegendes Grauerz über Tage”; see Anger et al. [1]), mostly consisting of barite and about 1% sulfides (mostly PbS) was decomposed in an oxygen atmosphere at 700°C and the sulfur-fraction released was precipitated as BaSO_4 by trapping the SO_2 in an acidified solution of 1N BaCl_2 . After addition of 1g of $\text{Fe/V}_2\text{O}_5$ flux to the residue the remaining sulfate-sulfur was liberated at a temperature of 1300°C and trapped in the same way. The precipitate then was converted to CdS (Kiba et al. [6]) and the sulfur isotopic composition was determined.

Table 1 shows the results obtained by this method in comparison to data from Anger et al. [1] who determined the $\delta^{34}\text{S}$ ratio at the same fractions, using the preparation technique described by Ricke [8]. The results show excellent coincidence and prove the application of the method described. Therefore, in geological samples the sulfide- and sulfate-sulfur amount and ratio may be defined by temperature. Of course, organically bound and elemental sulfur will become part of the sulfide fraction. But generally this sulfur fraction is of minor importance, being e.g. less than 2% of the total sulfur in recent marine sediments (Kaplan et al. [5]).

A large number of total-, sulfide- and sulfate-sulfur determinations were carried out by this method (Brumsack [2, 3]). In the range from 0.02–7.5% S the relative ‰ standard deviation was calculated to be less than 8% (Kaiser and Specker [4]).

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Simultaneous Iodometric Microdetermination of Iodide and Bromide Ions Using a 6-fold Amplification Reaction

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Iodometrische Simultanbestimmung von Iodid und Bromid durch eine 6fache Vervielfachungsreaktion

Key words: Best. von Iodid, Bromid; Volumetrie, Iodometrie; Vervielfachung

Simultaneous determination of iodate and bromate ions in aqueous solution using a direct titrimetric method has been reported [1, 2]. Trials to apply this procedure for the determination of iodide and bromide ions after oxidation to their halate ions were so far unsuccessful [3]. Stepwise examination of the reaction involved in this method indicates the great importance of the pH role in each step.

For quantitative oxidation of iodide and bromide ions with freshly prepared sodium hypochlorite, it was proved that the pH of the reaction mixture must be adjusted to 6–6.5. At lower pH-values (e.g., pH 4–5), quantitative oxidation of iodide to iodate was achieved but the oxidation of bromide ion was incomplete. Iodide and bromide ions could effectively be oxidized to their halates by adding 10 ml potassium dihydrogen phosphate solution (10%) followed by 4 ml of

freshly prepared 0.4N sodium hypochlorite (prepared by passing chlorine gas in 2N sodium hydroxide solution) and heating the solution near to boiling.

Formic, oxalic, malonic and succinic acids and sodium formate or oxalate were tested as destructing agents for the excess hypochlorite in the reaction mixture. Oxalic acid (10 ml of 30 mg/ml) was found to be the most suitable because this specified amount not only eliminates the excess hypochlorite but also brings the pH of the reaction medium to 3.8–4.1, which is very suitable for the next step. Excess solid potassium iodide was then added and iodine liberated which is only due the iodide-iodate reaction was titrated with sodium thiosulphate solution (0.01 N) in the presence of starch as indicator. The pH of the reaction solution was then lowered for about a unity by adding 5–7 ml of concentrated hydrochloric acid (20%) to allow the bromate-iodide reaction to take place and iodine liberated was also titrated with the thiosulphate solution.

This iodometric procedure can be used to determine 0.5–5 mg of each iodide and bromide with reasonable accuracy using this amplification reaction. Larger amounts of the halide ions could be determined but an increase in the hypochlorite concentration would be required.

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Rapid TLC Separation of Some Closely Related Arylazopyrimidinylpyrazoles

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Schnelle DC-Trennung einiger nahe verwandter Arylazopyrimidinylpyrazole

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Key words: Trenn. von Arylazopyrimidinylpyrazolen; Chromatographie, Dünnschicht

Arylazopyrazoles and pyrimidines have both been found to play an important role in the field of medicinal chemistry as they possess interesting antineoplastic or antidiabetic activity. Due to the key role of these compounds in medicinal chemistry, they have been separated by TLC [1, 2, 4] as this information may provide better understanding during drug evaluation. A large number of pyrimidinylpyrazoles have also been synthesised [3] by the combination of pyrazole and pyrimidine moieties so as to enhance the physiological and medicinal properties in all aspects. Keeping in view also the medicinal properties of arylazopyrimidinylpyrazoles it was