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Determination of Acid Volatile Sulfides in Sediment Samples Applying Cold Vapour Molecular Absorption Spectrometry

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We have applied molecular absorption spectrometry to the direct determination of acid volatile sulfides (AVS) in sediment samples. Sulfides were determined by measuring absorption of vapourized hydrogen sulfides. Gaseous hydrogen sulfide was generated by adding concentrated sulfuric acid. The accuracy was assessed by comparing the results with those obtained applying other methods, as well as for artificial samples. The lowest determinable concentration was 2 $\mu g\ g^{-1}$ and the corresponding sensitivity (A 1%) was 0.5 $\mu g\ g^{-1}$.

Do bezpośredniego oznaczania w próbkach osadów lotnych siarczków (AVS) uwalnianych pod wpływem kwasu, zastosowano cząsteczkową spektrometrię absorpcyjną. Siarczki oznaczano mierząc absorpcję siarkowodoru przeprowadzonego do fazy gazowej pod wpływem stężonego kwasu siarkowego. Dokładność metody oszacowano porównując otrzymane wyniki z wynikami uzyskanymi za pomocą innych metod jak również na drodze analizy próbek syntetycznych. Najniższe możliwe do oznaczenia stężenie wynosiło 2 $\mu g\ g^{-1}$, a czułość (A 1%) odpowiednio: 0.5 $\mu g\ g^{-1}$.

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Sulfur cycle in aquatic environment is the main factor determining mobility of metallic elements between sediments and water. Sulfides play the key role in this cycle. They are formed in anaerobic mineralization processes of organic matter or in microbial sulfate reduction. Hydrogen sulfide is generated in the first step of microbial reduction, in which bacteria decompose organic sulfur compounds, such as proteins – reaction 1:

$$\text{R–SH – bacteria} \rightarrow H_2S + HR \quad (1)$$

Microbes also participate in redox process of sulfate and carbohydrates (reaction 2):

$$SO_4^{2-} + 2H^+ + 2CH_2O \rightarrow H_2S + 2H_2O + 2CO_2 \quad (2)$$

Dissolved metallic elements are precipitated in the form of sulfides in the presence of H_2S [1–5]. The quantity of acid volatile sulfur (AVS) is a measure of the amount of easily available sulfide in sediments, most of which is in the form of amorphous FeS. AVS represents sulfides, which may react with dissolved heavy metals to form metal sulfide precipitates [6,7]. Furthermore, AVS can be regarded as a measure of sediment capacity to bind heavy metals and, in consequence, as a criterion of sediment quality [8]. AVS is defined as a fraction of sulfides extractable to cold hydrochloric acid. Determination of AVS is performed by acidification of the sample with hydrochloric acid (4–8 mol L^{-1}) in order to generate H_2S. Liberated H_2S is absorbed in various solutions and its amount is determined applying titrimetry, photometry, chromatography, and conductometry [1,3,9–11].

Currently used methods for the determination of AVS are often cumbersome, time-consuming, applicable only to liquid samples, and require different pretreatment techniques.

The purpose of this study was to develop fast and simple procedure for AVS determination in sediment samples for environmental control. The measurement was based on the direct determination of liberated H_2S applying molecular absorption.

Molecular absorption of H_2S cold vapour was first studied by A. Syty [12]. Absorption spectrum was recorded in the range 180–240 nm using a continuum irradiation source. In our previous study the continuum irradiation source was successfully replaced with a sharp-line source in order to increase sensitivity and accuracy of the determination. Different elemental lines from the range of maximum absorption of hydrogen sulfide were analyzed and finally selenium line at 196.0 nm was chosen as the one, which ensured the best results [13].

EXPERIMENTAL

Apparatus

Molecular absorption of H_2S was measured using a Perkin–Elmer 4100 atomic absorption spectrometer equipped with a 15 cm-in-length absorption cell. Experimental setup is shown in Figure 1. It was constructed after appropriate improvement of our earlier instrumentation system [14], mainly by optimizing gas volume by introducing an easily removable reaction tube. Measurements were performed at the wavelength of 196.0 nm corresponding to the absorption maximum of H_2S, using a selenium hollow-cathode lamp (Perkin–Elmer) as the irradiation source [13]. A LECO CS–344 combustion infrared analyzer and a Thermo Jarrel Ash Atomcomp 1100 inductively coupled plasma emission spectrometer were utilized in reference measurements. Mettler and Sartorius analytical balances and Mettler M3 microbalance (0–150 mg) were also used.

Materials

All reagents (Merck) were of pro-analytical grade. 10000 mg L^{-1} standard sulfide solution was prepared by dissolving $Na_2S{\cdot}9H_2O$ in distilled water containing 1% of NaOH (the solution was standardized by iodimetric titration). Working standard solutions of sulfide were prepared by appropriate dilutions of standard solution. Standard solid material was prepared by adding 5.0, 10.0 and 20.0 mg of potassium sulfide to 100 g of quartz (grain size < 2 mm) and homogenizing the components in the swing mill for one minute. Standard sulfide solutions and solid materials were prepared daily. Concentrated sulfuric and hydrochloric acids were used as the reaction solutions.

Procedure

Instrumentation used in the determination of H_2S is presented in Fig. 1. The sample was weighed in the reaction tube. After that, acidified reaction solution was injected into the tube in order to generate H_2S. The formed H_2S was introduced into the absorption cell in the stream of the carrier gas and the height of the absorption signal was measured. The volume of liquid standards and samples was 200 μL. The weighed portions of solid standards and samples were 0.01–1.0 g.

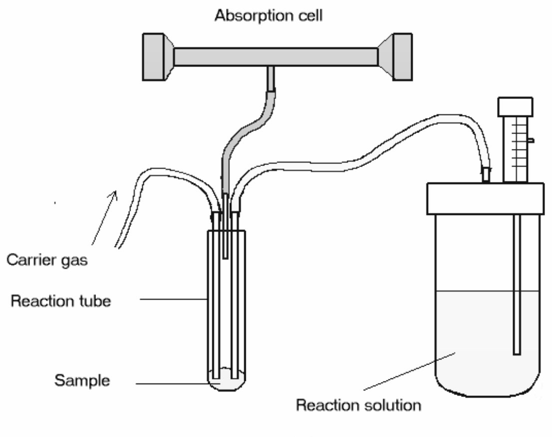

Figure 1. Experimental setup for H_2S generation and determination

Combustion infrared analysis and ICP–OES analysis of sulfur were performed as reference measurements. In the applied procedure, 1 g of the sample material was placed in a beaker, acidified with 1 mol L^{-1} HCl, and mixed for 20 min. During the waiting time, sulphide was evaporated and nitric acid was added. Finally, the sample was evaporated to dryness and dissolved using fuming nitric acid or *aqua regia*. Sulfur was determined applying ICP–OES method. Total sulfur concentration in the sample was determined by combustion infrared method, while ICP–OES method allowed one to determine only the amount of evaporated sulfur.

Reference method was validated by establishing the appropriate mixing time, so that volatile sulfides were totally evaporated after addition of the acid. Validation was performed using silicate samples, to which sodium sulfate and sodium sulfide were added. Sulfide was totally evaporated after 15 min, whereas in the reference method 20 min were required for complete evaporation. Evaporation step was performed by gentle heating so that the sulfate sulfur remained in the sample.

RESULTS AND DISCUSSION

Dead volume of the reaction system was minimized to 18 mL in order to provide maximum concentration of the formed H_2S. H_2S was generated in the reaction tube according to the below equation:

$$S^{2-}_{(aq)} + 2\,H^{+}_{(aq)} \rightarrow + H_2S_{(g)} \qquad (3)$$

This reaction was very fast and evolution of H_2S was immediate. Apart from different sulfuric acid solutions used to generate H_2S, also hydrochloric acid solution was used for this purpose (HCl is traditionally used in the determination of AVS). Figure 2 exhibits absorption signals measured under different conditions. The shape of the absorption peak depended on the flow rate of the carrier gas, as well as on the type of the absorption cell used. At high flow rates and opened absorption cell it was possible to obtain very sharp absorption peaks. In reference measurements absorption cell was equipped with „windows" at both ends, which led to wide peaks affected by significant tailing. Moreover, lower flow rates of the carrier gas also made the absorption peaks wider. In the presence of hydrochloric acid H_2S was generated at a slower rate and absorption signals were decreased twice compared to those recorded in the presence of sulfuric acid (at high flow rate of the carrier gas). Slower evaporation of H_2S caused also widening of absorption peaks, which were easily affected by even small changes in the flow rate of the carrier gas. However, the areas of absorption signals recorded under slow flow of the carrier gas were quite similar for both acids. At lower flow rates the absorption peak areas can be also calculated and determination of AVS can be performed. Then, however, it takes longer time for the signal to fully develop. Thus, it was preferred to shorten the analysis time as much as possible not to affect measured absorption signals at the same time. For the above practical reason, high flow rate of the carrier gas and strong sulfuric acid were applied. In order to optimize experimental conditions, different volumes of reaction solution were used. Reaction rate was decreased, when volumes smaller than 0.5 mL were used. The most reproducible results and the highest reaction rate were observed for the volumes of 1–2 mL. Having in mind these observations, 1 mL of the reaction solution was used in the determinations employing 0.01–1.0 g of the sample. Dry samples were moistened before adding the reaction solution. Injection of the reaction solution directly onto dry sample, in some cases, made the reaction proceed only on the surface and not within the entire sample volume, due to the formation of a surface cover which hindered the contact with the acid. Consequently, evolution of H_2S was decreased.

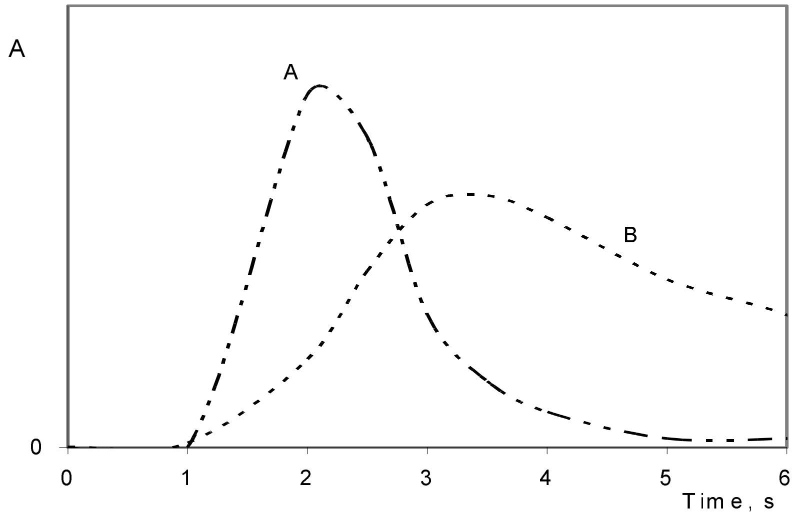

Figure 2. Absorption signal after addition of reaction solution. A – open absorption cell, high carrier gas flow rate; B – closed absorption cell and low carrier gas flow rate

Under appropriate conditions, reaction proceeded immediately after the solution was added. Flow rate of the carrier gas was adjusted to 6 L min^{-1}, in order to transport liberated H_2S to the absorption cell sufficiently fast. After one second since H_2S reached the absorption cell, the corresponding analytical signal was generated and measured. The recorded absorption signal is presented in Figure 2. Reaction time and mixing time (after addition of the reaction solution) were chosen to be as short as possible (*ca* 1 s). After this time, the carrier gas was introduced into the reaction tube. In some samples, at longer mixing times, liberated H_2S might be freely transported in the absorption cell and then absorption took place before the carrier gas flow was turned on. Consequently, lower and wider absorption peaks were observed. The above situation occurred especially in the case of artificial samples, in which sulfide concentration was very high. In these measurements, peak heights instead of peak areas were used to perform quantitative analysis, as H_2S was liberated quickly and repeatedly. The lowest determinable concentration of acid volatile sulfide was at a level of 2 μg g^{-1} and the corresponding sensitivity (A 1%) was 0.5 μg g^{-1}. The proposed method was fast and the time required for single analysis of the sample introduced to the reaction tube was 20 s. Within one hour, 20–30 samples could be analyzed.

The developed method was applied to the analysis of different kinds of soil samples. In the reaction tube 1 g of the sample was placed and the known amount of acid volatile sulfide was added. To the sample not containing sulfide, it was added in the form of sodium sulfide solution (5 to 20 μL). In the second step, sulfide was precipitated as FeS by adding iron nitrate to sodium sulfide solution. Then, the amount of produced AVS was measured. The results of these studies have definitely confirmed that sulfide totally precipitated as FeS, was evaporated as hydrogen sulfide after addition of sulfuric acid (Tab. 1). The obtained results are in a good agreement with earlier theoretical predictions.

Table 1. The results of determination of AVS in artificial samples (RSD obtained for six replicate determinations)

Type of sample	Sulfide Added, μg	Sulfide measured, μg	RSD %	Recovery %
Soil sample 1	8.0	8.5		106
Soil sample 2	12.5	12.0	6.3	96
Soil sample 3	25.0	25.6		102
Soil sample 4	50.0	48.0	3.8	96
Soil sample 5	120.0	112.0		93
Iron sulfide precipitated 1	1500	1320		88
Iron sulfide precipitated 2	1500	1450		97

Analysis of real samples

Real samples originated from rivulet sediment highly polluted with ores. Expected concentration of sulfide was 0.1–5% and the level of other contaminants, such as Cu and Zn, was between 100 and 500 mg kg^{-1}. Total sulfur was determined applying combustion infrared method (Leco). A part of non-volatile sulfur was determined by ICP–OES after dissolution of the sample in HCl and *aqua regia*. From the obtained results the amount of vapourized sulfide was estimated. The amounts of evaporated sulfides were overestimated in some cases, due to the possible dissolution of some heavy metals sulfides and subsequent evaporation of H_2S. Good agreement was found between the results concerning AVS determination between molecular absorption and reference method. In Tables 1 and 2 the results for different samples are presented; they indicate satisfactory accuracy and precision. In the case of real samples, their low homogeneity and different grain size caused deviations in analytical results.

Table 2. AVS concentrations determined in sediment samples contaminated by heavy metals (m/m%). The measurements were performed applying molecular absorption and ICP–OES/Leco

Sample	MAS %	Leco /ICP–OES %
S 1[a]	0.048 ± 0.009	0.06 ± 0.02
S 2[a]	0.051 ± 0.006	0.07 ± 0.03
S 3[a]	0.046 ± 0.007	0.04 ± 0.02
S 4[a]	0.020 ± 0.004	0.05 ± 0.01
S 5	0.035	0.05
S 6	0.045	0.06
S 7	0.052	0.04
S 8	0.031	0.04
M 1	0.021	0.02
M 2	0.010	0.02
M 3	0.008	0.02
M 4	0.035	0.03

[a] Averaged from six (molecular absorption) and three Leco/ICP replicate determinations; confidence level: 95%.

CONCLUSIONS

The proposed method based on molecular absorption of H_2S can be applied to the determination of AVS in different kinds of sediment samples. No special sample preparation is needed and the analysis time is short compared to traditional methods. Moreover, sensitivity and precision of the method are satisfactory.

The developed method is a simple and accurate analytical tool for practical determination of AVS. It does not require any special equipment and allows one to analyse a large number of samples.

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