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# SIMPLIFIED METHODS FOR THE DETERMINATION OF HYDROGEN SULPHIDE ACID IN SEDIMENT CONTAMINATED BY MINING ACTIVITIES

# UPROSZCZONE METODY OZNACZANIA KWASU LOTNYCH SIARCZKÓW W OSADACH SKAŻONYCH PRZEZ DZIAŁALNOŚĆ GÓRNICZĄ

## Abstract

The concentration level of hydrogen sulphide acid in the sediment contaminated by mining activities can be applied as criteria ability of sediments to bind the heavy metals and mobility of such metals. The determination of hydrogen sulphide acid (HSA) by molecular absorption spectrometry and combustion-IR analysis in sediment samples is described. The liberation of $H_2S$ is performed through the addition of the concentrated sulphuric or hydrochloric acid. The liberated hydrogen sulphide is measured directly using molecular absorption spectrometry (MAS) and by absorbing the HSA in a silver nitrate solution and measuring the precipitated sulphur by combustion (the IR method). The lowest determinable concentrations were at the level of 2–10 μg $g^{-1}$.

*Keywords*: *state of sediment*, *hydrogen sulphide acid determination*, *molecular absorption spectrometry*, *silver sulphide precipitation*

## Streszczenie

Lotny kwas siarki może być stosowany jako ilościowe kryterium jakości osadów wskazując ich zdolność wiązania metali ciężkich. Opisano możliwość oznaczania tego kwasu (AVS) w osadach metodą absorpcyjnej spektrometrii molekularnej i analizy spalania-IR. Wydzielanie siarkowodoru przeprowadza się przez dodanie stężonego kwasu siarkowego lub kwasu solnego. Uwalniany H2S jest mierzony bezpośrednio metodą molekularnej spektrometrii absorpcyjnej (MAS) jak również absorbując go w roztworze azotanu srebra i mierząc strąconą siarkę przez spalanie techniką IR. Najniższe możliwe do oznaczenia stężenia były w zakresie 2–10 µ $g^{-1}$.

*Słowa kluczowe*: *stan osadu, oznaczanie kwasu siarkowodorowego*, *absorpcyjna spektrometria molekularna*, *wytrącanie siarczku srebra*

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## 1. Introduction

The sulphur cycle in aquatic environments is generally the main factor controlling the mobility of metallic elements between the sediment and the water phase. In the sediments are the dissolved metallic elements as metal sulphides [1–5]. The amount of the acid volatile sulphur, $H_2S$, from the precipitated sulphides can be used as the determination method of easily available sulphide in sediment giving simultaneously indicating the mobility of the heavy metals [6–8]. Acid volatile sulphur is defined as the fraction of sulphide which is extractable by cold hydrochloric acid. The determinations of HSA are performed by liberating the $H_2S$ gas through acidification of the sample using hydrochloric acid (4–8 M). Generally, the formed hydrogen sulphide is absorbed in different solutions and determined by gravimetric, photometric, titrimetric, chromatographic and conductometric methods [1, 3, 9–12].

Current methods for the determination of HSA are often cumbersome, time consuming and generally require liquid samples and that is why different kinds of pre-treatment techniques are required.

The aim of presented study was to evaluate and develop quick and simple procedures to determine HSA in sediment samples for environmental control. These procedures are based on the liberation of HSA from sediment as $H_2S$ and its direct determination using gas phase molecular absorption, combustion IR – analysis, etc. [13–15].

## 2. Experimental Method

### 2.1. Apparatus

The molecular absorption of $H_2S$ was measured using a Perkin Elmer 4100 atomic absorption spectrometer with a 15 cm long absorption cell adjusted over the burner head. The system is described in Fig. 1 [15, 16]. For the measurements performed at the absorption maximum of $H_2S$ at 196.0 nm, the selenium hollow-cathode lamp (Perkin Elmer) was used as the irradiation source [16].

The other determination of HSA was performed through combustion infrared analysers LECO and ELTRA after the absorption of the liberated $H_2S$ and its precipitation by silver nitrate.

### 2.2. Materials

All the reagents were Merck pro-analytical grade. A standard sulphide solution (10000 mg $l^{-1}$) was prepared by dissolving $Na_2S{\cdot}9H_2O$ in distilled water containing 1% of NaOH (the solution was checked and standardised by iodometric titration). The working standard sulphide solutions and reference solutions were prepared by diluting this solution. The reference solid material was prepared by adding 5.0, 10.0 and 20.0 mg of sulphide in the form of potassium sulphide to 100 g of quartz (< 2 mm). The homogenisation was performed using the swing mill for milling the components for one minute in order to obtain a homogenous mixture. The standard and reference sulphide solutions and materials were prepared daily. The concentrated sulphuric or hydrochloric acid was used as the reaction solution.

### 2.3. Procedure

The experimental set-up for the determination of $H_2S$ by MAS is presented in Fig. 1. The sample was weighted in the reaction tube and subsequently, the acidic reaction solution was injected into the tube in order to liberate the $H_2S$ gas. After the reaction solution was added to the sample, the formed $H_2S$ was introduced into an absorption cell by carrier gas and the peak height of the generated absorption signal was measured. The volume of liquid standards and samples was 200 µl and the weights of solid standards and samples were between 0.01 and 1.0 g. For the liberation of $H_2S$ gas, 1 ml of the sulphuric acid reaction solution was used in the determinations for 0.01–1.0 g of sample. The flow rate of the carrier gas used was 6 l $min^{-1}$.

When the analysis was performed by absorption and precipitation of liberated $H_2S$ gas in the absorption tube by an $AgNO_3$ solution (0.1 M), the sample amounts were 10–20 ml or 5–50 g. As the reaction solution 10–30 ml of hydrochloric acid (6 M) was used. The formed $H_2S$ was transported to absorption tube by carrier gas. The precipitated silver sulphide was filtered and the dried filter was placed in the sample cup of the sulphur analyzer and routine analysis was performed. The procedure used in the liberation of $H_2S$ gas and its absorption is presented in Fig. 1.

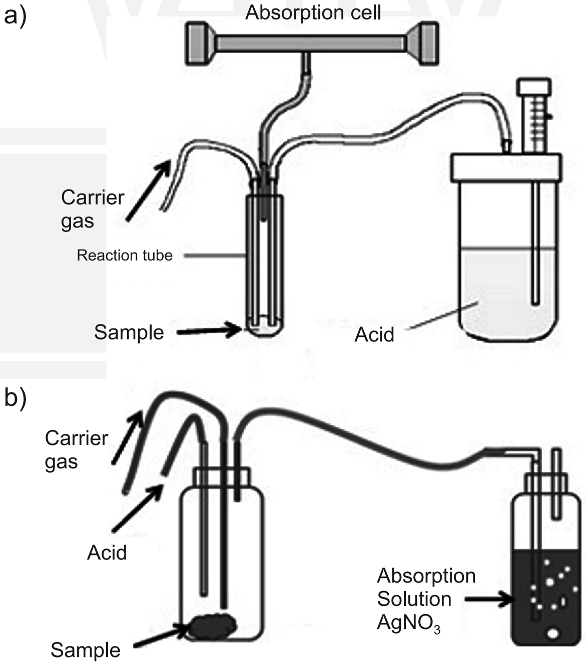

Fig. 1. The measurement systems: a) the system where the $H_2S$ is measured by molecular absorption and b) the system where the liberated $H_2S$ is absorbed and precipitated

## 3. Results and Discussion

### 3.1. The measurement of artificial samples

The basic reaction which describes the liberation of the $H_2S$ in the reaction tube is:

$$S^{2-}_{(aq)} + 2H^{+}_{(aq)} \rightarrow H_2S(g)$$

This reaction is very fast and the liberation of $H_2S$ is immediate. In the liberation of $H_2S$, a sulphuric acid solution was used in addition to a hydrochloric acid solution that has been traditionally used in the determination of HSA. The dry samples had to be moistened before adding the acid solution, because when the acid is injected onto the dry sample, in some cases, only the surface reacts forming a cover under which the remaining part of the sample only slowly gets into contact with the acid causing slower evaporation of $H_2S$. Under correct conditions, the reaction is immediate following the addition of the reaction solution.

In the case of the MAS method, the dead volume of the reaction system together with the connection to the absorption cell has been minimised at 18 ml in order to keep the concentration of the formed $H_2S$ in the absorption measurement cell as high as possible. The shape of the absorption peak was dependent upon the flow rate of the carrier gas as well as on the type of the absorption cell used. With the high flow rate and open absorption cell, it was possible to obtain very sharp absorption peaks. In the case of using the hydrochloric acid instead of sulphuric acid as the reaction solution, a slower liberation of $H_2S$ was observed. The absorptions were about half of size of those obtained with the use of sulphuric acid (peak height was taken into account in determination). When the determinations were performed by measuring the area of the absorption signal, the results were quite similar for both of the acids.

Sulphuric acid was selected as the reaction solution in the MAS measurement for practical reasons, because by that procedure, a repeatable and stable absorption signal was obtained which allowed for the shortest measurement times. In the case of the MAS procedure, the flow rate of the carrier gas which brings the liberated $H_2S$ to the absorption cell, was selected to be 6 l min$^{-1}$. At this rate, the $H_2S$, after one second in the absorption cell, gives an adequate signal for its the determination.

The reaction and mixing time after the addition of the reaction solution was chosen to be as short as possible, about one second, after which the gas flow was introduced into the reaction tube. In these measurements, the peak height for quantification was because the liberation of $H_2S$ is quick and repeatable. The lowest determinable concentration of acid volatile sulphide by the MAS procedure was at a level of 2 μg g$^{-1}$ and the corresponding sensitivity (A 1%) was 0.5 μg g$^{-1}$. The method is quick and the time required for one determination, after the sample has been measured to the reaction tube, is 20 seconds. Within one hour, 20–30 samples can be completely and easily measured.

When the method that is based on the absorption of the liberated $H_2S$ in the absorption solution the reaction speed and gas flow rate are not critical same it is possible to use bigger sample amounts those demand only increase of the added acid volume. Hydrochloric acid (6 M) was used as the reaction/liberation solution and the liberated $H_2S$ was absorbed in the silver nitrate solution where silver sulphide was formed and precipitated.

The precipitated silver sulphide was filtered, drying and sulphur analysis was performed by the combustion infrared method. The detection limit of the method lies at a level of 10 µg of S.

The developed method was first tested by different kinds of soil and mineral samples by adding the known amounts of hydrogen sulphide acid as sodium sulphide to the reaction tube with one to ten gram of sample (Table 1). The results of measurements were in a good agreement with the theoretical values. As the mineralised form of the sulphides they have not anymore capacity to bind heavy metals from water, therefore they were tested as freshly milled sulphide ores (Cu-Ni and pyrite). As expected, the amount of $H_2S$ separated from the ore gave less than 0.1% of the total amount of sulphides.

Table 1

**The results of determination of HSA from artificial samples by MAS and combustion – IR absorption method after precipitation**

| Sample | Sulphide added µg | MAS µg | precip- abs.-Eltra µg |
|---|---|---|---|
| 1 | 20 | 20.5 | 20.7 |
| 2 | 50 | 48.0 | 50.8 |
| 3 | 100 | 95.3 | 101.7 |
| 4 | 200 | 184.0 | 199.4 |
| 5 | 500 | 483.3 | 514.6 |

Table 2

**HSA concentrations measured in sediment samples contaminated by mining activities. The measurements were performed by molecular absorption and by absorption-precipitation – combustion IR (Eltra) methods**

| Sample | MAS µg/mg | Precip.- abs.-Eltra µg/mg |
|---|---|---|
| S 1 | 3.3 | 4.7 |
| S 2 | 6.5 | 5.2 |
| S 3 | 11.9 | 15.8 |
| S 4 | 14.8 | 16.7 |
| S 5 | 21.4 | 23.8 |
| S 6 | 24.8 | 24.1 |
| S 7 | 25.8 | 26.8 |
| S 8 | 34.5 | 37.4 |
| S 9 | 35.3 | 41.6 |
| S 10 | 35.4 | 33.1 |

### 3.2. The measurement of real samples

The tested samples were origin from the sediment heavily polluted by handling of ores where the mineral concentrations was between 0.1–5 % and the level of the contaminants such as Cu and Zn between 100 and 500 mg kg$^{-1}$. As the reference the total sulphur was measured by combustion infrared method and the part of non-volatile sulphur by measurement after the treatment of the sample with HCl. From those results, the amount of vaporised sulphide sulphur was estimated. The good agreement was found between the results obtained by molecular absorption and the precipitation-combustion IR method with those obtained by the reference combustion IR method that was used in order to get the level of acid volatile sulphide in the samples. Tables 1 and 2 present the results obtained in the determination of the different samples where it can be seen that the accuracy of the results obtained are sufficient. In the case of the real samples, their low homogeneity and different sizes of solid particles caused deviation in the analytical results.

## 4. Conclusions

The quickly determination of acid volatile sulphides represents a good consider changing ‘good’ to more ‘practical’ method for evaluating the state of the sediment including its ability to bind the heavy metals and evaluate their mobility. For the determination of HSA in different kinds of sediment samples, the studied methods where the liberated $H_2S$ is measured either directly by molecular absorption or it is absorbed in solution by precipitation and determined by combustion IR method are providing good analytical tools and practices. No special sample preparation is needed and the time consumption of the analysis is much lower than in traditional methods. The pieces of analytical equipment needed are an atomic absorption spectrometer or a combustion IR analyser – both of these are basic pieces of equipment in every mine laboratory. It was shown that the sensitivities and precision of the methods are satisfactory. The experimental results suggest that for the determination of HSA, these simple and accurate methods would provide a good analytical tool for practical reasons.

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