ISSN 1063-455X, Journal of Water Chemistry and Technology, 2015, Vol. 37, No. 6, pp. 289–294. © Allerton Press, Inc., 2015.
Original Russian Text © O.A. Zaporozhets, O.S. Pogrebnyak, A.S. Paustovska, 2015, published in Khimiya i Tekhnologiya Vody, 2015, Vol. 37, No. 6, pp. 526–536.

ANALYTICAL CHEMISTRY OF WATER

Indirect Spectrophotometric Determination of Sulphides with N,N-Dietylaniline

O. A. Zaporozhets*, O. S. Pogrebnyak, and A. S. Paustovska

Shevchenko National University, Kiev, Ukraine

**e-mail: pogrebniak-oleg@ukr.net*

Received September 15, 2015

Abstract—Proposed is the technique of spectrophotometric determination of sulfide in the range 0.05–1.50 mg/dm^3 based on oxidation of it in the sulfate medium by the known excess of bromate followed by subsequent oxidation of N,N-diethylaniline in the presence of the excess of bromide and photometering at 226 nm of 4-bromo-N,N-dietylaniline being formed. The sulfide detection limit constitutes 0.03 mg/dm^3. Metrological characteristics of the technique were checked by way of determination of sulfide in waters in ballneotherapy (mud, silt, etc.).

DOI: 10.3103/S1063455X15060053

Keywords: bromate, bromide, N,N-diethylaniline, spectrophotometry, sulfide.

INTRODUCTION

Sulfides are the feedstock for the production of non-ferrous metals, colorants, dyes and sulfuric acid: they are formed at purification of industrial gases of hydrogen sulfide [1]. Sodium sulfide is used for obtaining sodium thiosulfate, hydroxide, hydrosulfide and soda as well as in leather-and-boot and textile industries. Together with wastewaters of the indicated industries sulfides get into the environment and when it penetrates a human organism it may cause serious or even deadly poisoning [2]. At the same time slime sulfide muds thanks to a unique combination of organomineral complex, microelements and other biologically active substances are used with medicinal purposes.

Iodometric and spectrophotometric methods are standard for the control of the content of sulfides in various objects; these methods in the base of the last one lies the reaction of the formation of methylene blue [3]. Given relative simplicity and accessibility the titrimetric technique is insufficiently sensitive and little selective. The spectrophotometric method is characterized by greater sensitivity and selectivity, but its main setback is labor intensivity and duration (up to 40 min).For determination of sulphur sulfides methods were also proposed described in references [2, 4–10]. Chronopoteniometric [4], voltamperometric [2, 5] and kinetic [6, 7] methods are characterized by low reproducibility, precision, require hiring of highly skilled personnel and the use of high purity reagents.

Known extraction-spectrophotometric methods [8–10] are ecologically unsafe due to the necessity of using cyanide and organic solvents. Determination of sulfides by their own light absorption in ultraviolet [11] is little selective. A detailed analysis of methods of determination of sulfides is given in [12].

Thus, despite the variety of proposed approaches the problem of developing a simple, expressive and simultaneously sensitive and ecologically safe technique of determination of sulfides in complex objects is important.

It is known [13] that N,N-diethylaniline (DEA) in acid medium is a bromide-bromate mixture with the formation of 4-brome-N,N-dietylaniline, which was placed as a basis of spectrophotometric determination of bromate, therefore the objective of the present paper is investigation of this reaction for indirect spectrophotometric determination of sulfides.

EXPERIMENTAL

We used freshly distilled at 217°C DEA, qualification “pure” of sodium sulfide (“pure for analysis”, all other reagents were “chemically pure”). Reagents were prepared using bidistilled water. A mixed reagent (MR) contained 0.1 mol/dm^3 of DEA, 0.01 mol/dm^3 of KBr and 4.8 mol/dm^3 of H_2SO_4. The initial solution of $KBrO_3$ (0.01 mol/dm^3) was prepared by accurate weighted quantity, while the working solution (3.5×10^{-4} mol/dm^3

by diluting the initial solution. The oxidizing blend (OB) contained 3.5×10^{-4} mol/dm^3 of $KBrO_3$ and 1.6 mol/dm^3 of H_2SO_4.The initial solution of sulfide was prepared by dissolving the weighted quantity of $Na_2S \cdot 9H_2O$ in water. Accurate concentration was set iodometrically according to [3]. The working solution of sulfide (5.0 m/dm^3) was prepared directly before conducting the experiment by diluting the initial solution and stabilized by adding zinc acetate [14].

Absorption spectra and optical density of solutions were registered by a spectrophotometer Helios γ v7.03 (Thermo Spectronic, Great Britain). For stirring and heating of solutions a magnetic agitator MM-5 was used (Mukachevo Plant of Complex laboratories, Ukraine). Samples of silts of OAO Cherkassy Khimvolokno and mud of Saki lake were dried in a drying cabinet SNOL-3.5 (Homel ZIP, Belarus).

With the aim of determination of optimal acidity of the reaction mixture a 0.5 cm^3 of the working solution of sulfide was added 1.0 cm^3 of sulphuric acid of certain concentration, 0.5 cm^3 of the working solution of bromate held for two or three minutes at 23 ± 2°C and introduced 2.0 cm^3 of MR. The resultant blend was held for the same time at 80 ± 5°C. The optical density of solutions was registered at 26 nm against the comparison solution, which was MR diluted with bidistilled water at the ratio 1 : 1. Its optical density in water constituted 1.9.

For identification of the final product of oxidation of sulfide by bromate chemical glasses of 10.0 cm^3 were filled with various volumes of sulfide (1.0×10^{-4} mol/dm^3) and brought to 1.0 cm^3 by bidistallator. Added 1.0 cm^3 of the solution $KBrO_3$ (3.5×10^{-4} mol/dm^3), which contained 1.6 mol/dm^3 of sulfuric acid. After 5 minutes we introduced 2.0 cm^3 of MR, mixtures were heated for two-three minutes up to 80 ± 5°C, cooled to room temperature and registered optical density at 226 nm. As a comparison solution we used a solution prepared by mixing 2.0 cm^3 of MR and 2.0 cm^3 of bidistillate.

For establishing time necessary for completion of the reaction, mixed 1.0 cm^3 of the working solution of sulfide with 1.0 cm^3 of OM, held if for 0; 1; 2; 3; 5; 10 and 15 min at 23 ± 2°C and introduced 2.0 cm^3 of MR. Mixtures were held for two–three minutes at 80 ± 5°C, then solutions were cooled to room temperature and registered optical density at 226 nm against the comparison solution prepared mixing 2.0 cm^3 of MR, 1.0 cm^3 of OM and 1.0 cm^3 of bidistillate. Its optical density with respect to water is 2.1.

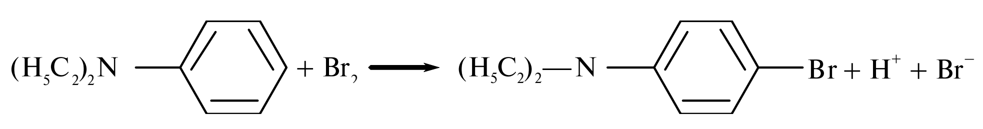
To construct a graduation graph (GG) glasses, capacity 10.0 cm^3, were filled with 0.1 to 1.0 cm^3 of the working solution of sulfide, added bidistillate to the total volume of 1.0 cm^3 and introduced 1.0 cm^3 of OM. Mixtures were held for five minutes at 23 ± 2°C, introduced 2.0 cm^3 of MR then held for two-three minutes at 80 ± 5°C, cooled to room temperature and registered light absorption of solutions at 226 nm. As a comparison solution we used a solution prepared by mixing 2.0 cm^3 of MR, 1.0 cm^3 of OM and 1.0 cm^3 of bidistillate.

When investigating the impact of foreign ions on determination of sulfide glasses of 10.0 cm^3 were filled with 0.5 cm^3 of the solution of sulfide (5.0 mg/dm^3), added 0–0.5 cm^3 of the solution of salts, a bidistillate to 1.0 cm^3 and 1.0 cm^3 of MR. Mixtures were held for five minutes at 23 ± 2° C, added 2.0 cm^3 of MR and held for two–three minutes at 80 ± 5°C, Cooled to room temperature and registered light absorption of solutions at 226 nm. Selectivity coefficients (K_s) were calculated by the formula $K_s = C(X)/C/S^{2-})$, where $C(X)$ and $C(S^{2-})$ are molar concentrations of respectively sulfite and strange ion, whereby an error of determining sulfide did not exceed 5%.

RESULTS AND DISCUSSION

Earlier we showed that oxidation of DEA by the bromide–bromate mixture in an acid medium is accompanied by the formation of 4-brom-N,N-dietylanine:

$$5Br^- + BrO_3^- + 6H^+ = 3Br_2 + 3H_2O; \quad (1)$$



(2)

In this case maximum difference of optical density of solutions (ΔA) is observed at 226 (Fig. 1).

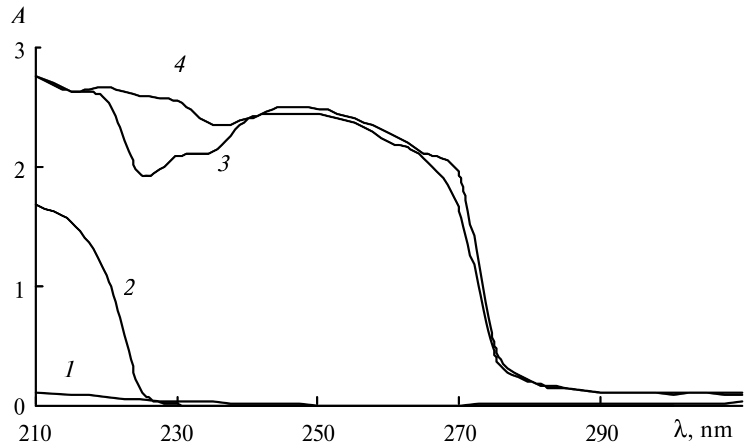


Fig. 1. Absorption spectra of initial substances and the reaction product: *1*—$KBrO_3$, *2*—KBr, *3*—DEA, *4*—Br–DEA. Concentration of reagents, mol/dm^3: $KBrO_3$—8.8×10^{-5}; KBr—5×10^{-3}; DEA—5×10^{-2}; Br-DEA—2.6×10^{-4}. $l = 1.0$ cm; comparison solution—water.

It was found that maximum ΔA_{226} is observed at the concentration of H_2SO_4 in a range of 0.75–0.85 mol/dm^3. In Fig. 2 it is seen that under these conditions in the diagram of molar relations the inflection point corresponds to the molar ratio bromate/sulfide constituting 1.33, which is an evidence of oxidation of sulfide to sulfate. With the account of indexes of constants of dissociation of reagents (for H_2S $pK_{a1} = 7.2$, $pK_{a2} = 14.0$; $HBrP_3$ $pK_a = 0.7$; H_2SO_4 $pK_{a1} = 1.9$ [15]) the equation of the reaction of oxidation of sulfide may be represented in the following way:

$$4HBrO_3 + 3H_2S = 4Br^- + 3HSO_4^- + 7H^+. \quad (3)$$

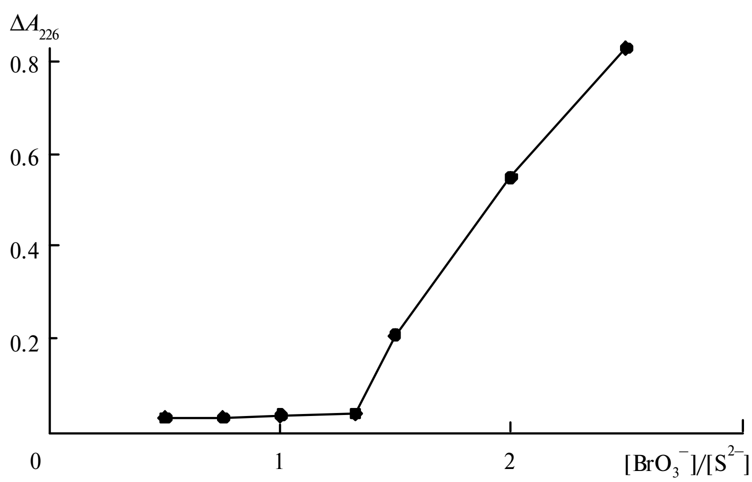


Fig. 2. Relationship between the optical density 0.05 mol/dm^3 of the DEA solution in the presence of 5×10^{-3} mol/dm^3 KBr in 0.8 mol/dm^3 of H_2SO_4 and molar ratio bromate/sulfide at 23°C. $l = 1.0$ cm; duration of holding mixtures—five minutes; comparison solution—all components except sulfide.

Results of investigation of the impact of the time of holding the reaction mixture $H_2S + KBrO_3 + H_2SO_4$ on the analytical signal are given in Fig. 3. When blending this solution with DEA in the presence of bromide that did not react with sulfide bromate forms Br_2 which enters into reaction with DEA.

The GG equation has the form:

$$\Delta A_{226} = 0.377 \pm 0.006 \cdot C(S^{2-}),$$

where C is the concentration of sulfide, mg/dm^3.

Sulfide detection limit constitutes 0.03 mg/dm^3. Linearity of GG is preserved within interval 0.05–1.50 mg/dm^3.

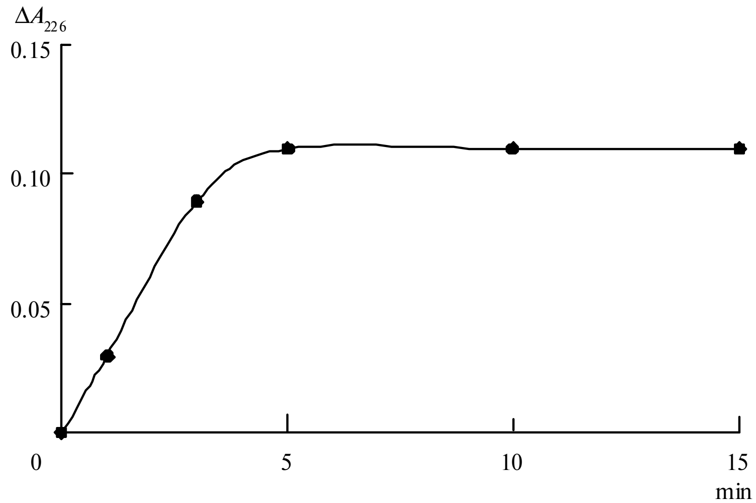


Fig. 3. Relationship between the optical density 0.05 mol/dm^3 of the DEA solution in the presence of 3.9×10^{-5} of H_2S and 8.8×10^{-5} mol/dm^3 $KBrO_3$ in 0.8 mol/dm^3 of H_2SO_4 at 23°C and the duration of holding the reaction mixture, $l = 1.0$ cm; the comparison solution—all components except sulfide.

Aqueous solutions with different content of S^{2-} were analyzed. From Table 1 it is seen that the developed technique is characterized by satisfactory correctness and convergence; relative standard deviation does not exceed 0.09.

Table 1. Results of determination of sulfades in aqueous solutions ($l = 1.0$ cm; $P = 0.95$; $n = 7$)

Content S^{2-}, mg/dm^3		S_r
introduced	found $x \pm \Delta x$	
0.4	0.4 ± 0.1	0.09
1.2	1.2 ± 0.1	0.08

Results of investigation of the impact of foreign ions are given in Table 2 from which it may be seen that ions NH_4^+, Zn^{2+}, Cl^-, Br^-, phosphate and acetate more than in 10-fold amounts do not impede the determination of sulfide. Determination is impeded by Cu^{2+} and Pb^{2+}, which form with sulfides insoluble deposits ($SP_{FeS} = 5 \times 10^{-18}$, $SP_{CuS} = 6.3 \times 10^{-36}$, $SP_{PbS} = 2.5 \times 10^{-27}$) [15] and also oxidizers Fe^{3+} and NO_3^-. The impeding impact of nitrate, in addition, is determined by its strong light absorption at 226 nm [16]. Thus, the proposed technique is suitable for determining equilibrium concentration of sulfide in many natural objects.

Table 2. Impact of foreign ions when determining 1.95×10^{-5} mol/dm^3 of sulfide

Ion	K_c	Ion	K_c
$H_2PO_4^-$	6400	CH_3COOH	44
NH_4^+	5100	Cu^{2+}	4.3
Cl	435	Pb^{2+}	2.5
Zn^{2+}	88	NO_3	0.8
Br	44	Fe^{3+}	0.8

It should be noted at that sulfides are widely used in production of artificial silk. At the AOA Cherkassy Khimvolokno Plant sulfides are used for binding Zn(II). Deposit that is formed is accumulated in the form of silt.

All-slime sulfide muds are organomineral thin-dispersion deposits of silt of salt water bodies the content of hydrogen sulfure and iron(II) sulfide are present in lake, continental, coastal and marine water bodies, in particular near the banks of the Saki lake (the Crimea). Soluble sulfides also display medicinal effects and are used as baths (100–159 mg/dm^3).

Determination of Sulfide in Waters of Balneobaths

Samples were diluted 100-fold. 1.0 cm^3 of diluted solution was added with 1.0 cm^3 of OB held for five minutes at 23 ± 2° and introduced 2.0 cm^3 of MR the resultant mixture was held for two or three minutes at 80 ± 5°C. Optical density of solutions was registered at 226 nm against the comparison solution prepared by mixing 2.0 cm^3 of MR, 1.0 cm^3 of OB and 1.0 cm^3 distilled water. The concentration of sulfide in samples was also controlled iodometrically [3].

Determination of Sulfide in Silt of OAO Cherkassy Khimvolokno Plant and Medicinal Mud of the Saki Lake

A weighted quantity of the sample (100.0 g) was dried in a drying cabinet to constant mass at 100 ± 5°C. The weighted quantity of the dry sample of 1.00 g was placed in a Wurtz flask, then added 20.0 cm^3 of distilled water, 5.0 cm^3 of concentrated sulfuric acid and heated the mixture to boiling. Gases that were released as a result of the reaction were absorbed by 10.0 cm^3 of a 1.0 mol/dm^3 solution of NaOH. The resultant solution was filtered through a loose ashless filter; 1 cm^3 of a 10% solution of cadmium acetate was added to the filter. A deposit that was formed of CdS was filtered, washed with distilled water, transferred quantitatively to a measuring flask and brought by distilled water to mark. Further determination of sulfide was conducted as specified above.

Results of sulfides determination in objects being analyzed are given in Table 3 from which it is seen that data obtained according to the proposed technique satisfactory agree with such obtained by the iodometric method.

Table 3. Results of determining sulfide in objects being analyzed. ($P = 0.95$; $n = 5$)

Objects	Standard technique			Proposed technique		
	found S^{2-}, mg/dm, $x \pm \Delta x$	S_r	V	found S^{2-}, mg/dm^3, $x \pm \Delta x$	S_r	V
Medicinal baths*	96 ± 6	0.05	17	95 ± 5	0,04	15
Silt of OAO Cherkassy Khimvolokno	896 ± 56	0.06	2048	856 ± 51	0.05	1704
Medicinal muds of the Saki lake	64 ± 11	0.14	82	58 ± 6	0.09	25

*Content (mg/dm^3): H_2S—100–50, $NaHCO_3$—135–270, NaCl—5100–7600.

The convergence of results obtained with the developed technique are somewhat higher since the value of dispersion in such a case is smaller. The difference according to Fisher's criterion is statically insufficient value. Consequently, both samplings belong to one general combination and results spectrophotometric and titrimetric determination may be considered as results of one sampling. Thus, the developed technique may be recommended as alternative for determination of the content of sulfides in various objects of the environment.

CONCLUSIONS

The technique is characterized by satisfactory sensitivity and selectivity, sufficiently simple in execution and ecologically safe, while reagents are accessible and stable in storage. Compared with a standard titrimetric technique [3] the proposed technique is more selective substance capable of oxidizing in an acid medium iodide to iodine and compared to a standard spectrophotometric one [3] is more expressive. Results of its testing in analyzing a series of complex objects are an evidence of satisfactory accuracy and convergence.

REFERENCES

1. Pozin, M.E., *Tekhnologiya mineralnykh solei: v 2 t.* (Technology of Mineral Salts), Leningrad, Khimia, 1974, vol. 2, pp. 466–470.
2. Lawrence, J., Robinson, K.L., and Lawrence, N.S., *Anal. Sci.,* 2007, vol. 23, pp. 673–676.
3. *OST 39-234-89. Voda dlya zavodneniya neftyanykh plastov. Opredelenie soderzhania serovodoroda.* (OST 39-234-89. Water for flooding oil beds. Determination of Content of Hydrogen Sulfide), introduced on July 1, 1990, pp. 4–7.
4. Manova, A., Strelec, M., Cacho, F., Lehotay. J., and Beinrohr, E., *Anal. Chim. Acta.,* 2007, vol. 588, no. 1, pp. 16–19.

5. Prodromidis, M.I., Veltsistas, P.G., and Karayannis, M.I., *Anal. Chem.,* 2000, vol. 72, no. 17, pp. 3995–4002.
6. Afkhami, A., Sarlak, N., Zarei, A.R., and Madrakian, T., *Based. Kor. Chem. Soc.,* 2006, vol. 27, no. 6, pp. 863–868.
7. Barzegar, M., Jabbari, A., and Esmaeili, M., *Ibid.,* 2003, vol. 24, no. 9, pp. 1261–1264.
8. Koh, T., Takahashi, N., Yamamura, N., and Miura, Y., *Anal. Sci.,* 1993, vol. 9, no. 4, pp. 487–492.
9. Miura,Y., Fukisaki M., and Haddad, P.R., *Ibid.,* 2004, vol. 20, pp 363–367.
10. Shanthi, K. and Balasubramanian, N., *Analyst.,* 1996, vol. 121, pp. 647–650.
11. Eremin, Yu.G. and Kiselev, K.S., *Zhurn. Analit. Khimii*, 1969, vol. 24, no.8, p. 1201.
12. Nathan, S., Lawrence, J.D., and Compton, R.G., *Talanta.,* 2000, vol. 52, no. 5, pp. 771–784.
13. Zaporozhets, O.A., Pogrebnyak, O.S., and Vizir, M.M., *Methods and Objects of Chemical Analysis,* 2009, vol. 4, no. 1, pp. 48–55.
14. Lur'ye, Yu.Yu., *Analiticheskaya khimiya promyshlenykh stochnykh vod* (Analytical Chemistry of Industrial Wastewaters), Moscow: Khimiya, 1984, p. 296.
15. Rabinovich, V.A. and Khavin, Z.Ya., *Kratkiy khimicheskii spravochnik* (Short Chemical Guide Book), 1991, pp. 265–266.
16. Williams, W.J., *Determination of Anions,* Moscow: Khimiya, 1982.

Translated by A. Koziy