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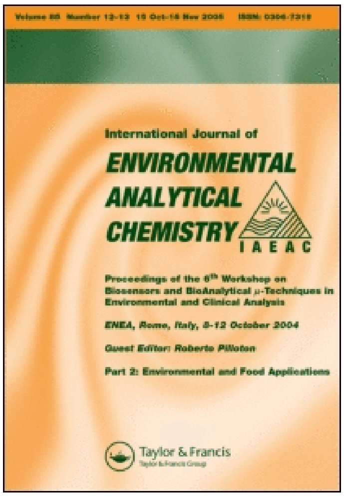

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A COMPARATIVE STUDY OF SPECTROPHOTOMETRIC AND IODOMETRIC BACK TITRATION METHODS FOR HYDROGEN SULFIDE DETERMINATION IN ANOXIC BASINS

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Iodometric Back Titration (IBT) and Spectrophotometric (SPM) methods are two common methods used in the determination of hydrogen sulfide concentrations in anoxic basins, like in the upper sections of the Black Sea anoxic waters. Although the results obtained by both methods are in agreement when the concentrations of sulfide are higher than 30 μM/l, IBT analysis gives more reproducible results compared to SPM analysis. On the other hand, the reproducibility of the SPM is better than that of IBT method when the concentration of sulfides is less than 30 μM/l, but in this case SPM method provides lower results compared to IBT method. This discrepancy can be explained by the presence of the hydrogen sulfide oxidation products (i.e., thiosulfate) formed as a result of aeration of water samples. These products consume the iodine added to the sample. Therefore, they are measured as hydrogen sulfide in the IBT method, but are not detected by the SPM method since they do not react with the N,N-dimethyl-p-phenylendiamine – $FeCl_3$ mixed reagent.

Keywords: Spectrophotometric; iodometric; comparison; Black Sea; hydrogen sulfide

INTRODUCTION

Hydrogen sulfide, a key chemical parameter for any anoxic marine environment, is very abundant in Black sea waters where its onset varies from the depths of 70–80 m in the interior of the basin to 200–250 m at the periphery[1]. There are three methods that are practically applied for the determination of hydrogen sulfide in anoxic basins, namely, Iodometric Back Titration (IBT)[2,3], Spectrophotometry (SPM)[4–6], and Voltammetry [7]. Contradictory results related to the

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spatial and temporal variations in the position of the oxic/anoxic transition zone which depends, particularly, on the accuracy of hydrogen sulfide determination, have led us to perform *in situ*comparison experiments for the analysis of this parameter by two methods, IBT and SPM.

The majority of the hydrogen sulfide data for the Black sea has been obtained by the IBT method[3,8] due to its simplicity. Since the IBT method is a non-selective method, all reduced sulfur species including H_2S which react with the iodine added to the samples and will be measured as "hydrogen sulfide"[1–3]. About 80% of all the iodine-reactive, reduced sulfur species was shown to be composed by sulfide (S^{2-}) and hydrosulphide (HS^-); whereas the undissociated form (H_2S) contributes less than 20% of the total hydrogen sulfide even at depths of 2000 m[1]. Only a small fraction of the total reduced sulfur species is made up by the thiosulfate ($S_2O_3^{2-}$), elemental sulfur (S^0), sulfite (SO_3^{2-}), polysulphides (S_x^{2-}), and poly-thionates[1,7,8,9]. Sub-surface S^0 maximum was detected only at depths just below the sub-oxic/anoxic interface of the Black Sea[10]. On the other hand, Yao and Millero[11] found that elemental sulfur (S°) is the dominant product of oxidation of H_2S both by Fe(III) hydroxides and MnO_2. Studies of Ciglenecki and Cosovic[12] within the fotic zone of the Adriatic sea have also shown the possibility of stabilisation of sulfur elements by organic matter and some metal sulfides in oxic waters.

In general, the precision of IBT method is given as ±3%[13]except in the upper parts of the anoxic zone where the concentration of hydrogen sulfide is less than 10 μM.

Some investigators[5,14–16] have been using SPM method for the determination of hydrogen sulfide in Black Sea waters due to its simplicity and high sensitivity. It has been claimed that the SPM method is selective only for the sulfide partitioned as H_2S, HS^- and S^{2-} in anoxic waters in the presence of other reduced sulfur forms[1,4,6,17]. The precision of this method for replicate sulfide analyses of artificial Na_2S solutions is given as ±2% at the 95% confidence level[5].

Even though the SPM method is more convenient and sensitive than the IBT method, there are some conflicting conclusions when the results obtained by the IBT and SPM methods are compared. Gaines and Pilson[18] reported a good agreement between the results obtained by both methods in estuarine waters where the total sulfide concentration was in the range of 160 to 4530 μM. However, Lukashov[19] showed that the SPM method was the best choice when the concentrations of hydrogen sulfide are less than 1 ml/l (≈ 45 μM), whereas significantly worse results were obtained by the SPM method when H_2S concentration is higher than 45 μM.

On the contrary, comparison of the data obtained by different investigators from the anoxic waters of the Black Sea have led Bezborodov and Eremeev[20] to

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conclude that the SPM method leads to higher values when the hydrogen sulfide concentration is higher than 50 μM. This result conflicts with that of Lukashov[19]. However, after analysing 57 water samples from the upper zone of the anoxic layer where H_2S concentrations varied in the 0–50 μM range, Novosjolov et al.[17]found no difference between the depth of hydrogen sulfide chemocline determined by both methods. Any observed difference in concentrations obtained by both methods has been attributed to the presence of thiosulfate[15]. This suggests that both methods are in good agreement for low H_2S concentrations. Therefore, both method can be equally used for detecting the sub-oxic/anoxic boundary in the Black Sea. However, when IBT and SPM data published by Novosjolov et al.[15] are re-plotted (Figure 1), one can see that the slope of the $[H_2S]_{SPM}$ versus $[H_2S]_{IBT}$ linear regression curve is 0.761, except in the range where the hydrogen sulfide concentration is less than 5 μM. It is rather difficult to attribute such a coherent difference (25%) from the ideal slope of 1.00 to the presence of thiosulfate, and other intermediate oxidation products of sulfur.

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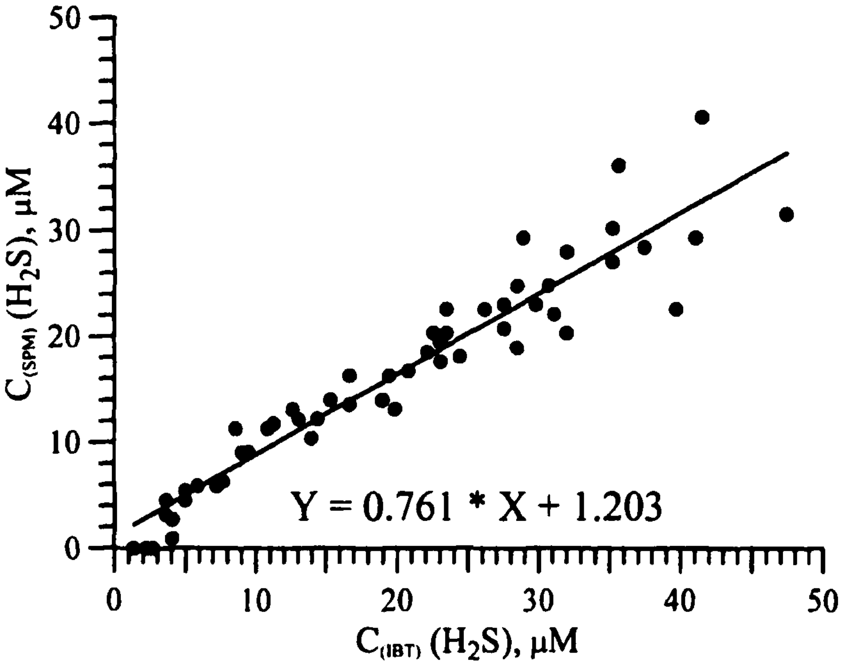

FIGURE 1 Plot of H_2S data measured by SPM and IBT methods in the Black Sea. (Based on the data of Novosjolov, et al.,[15])

Since different investigators obtained contradictory results and conclusions derived from these two methods, a field experiment has been conducted for clarification of the indicated problems, and to form a basis for the comparison and thus the correction of the results obtained by the IBT and SPM methods in the past.

EXPERIMENTAL

The SPM[6] and IBT[1] methods were run in parallel samples for H_2S analyses in anoxic waters of the Black Sea during joint cruises of *R/V Bilim* (IMS) and *R/V Professor Kolesnikov* (MHI) in March 1995, and under laboratory conditions. The iodine/thiosulfate ratio in the IBT method, used in calculating the H2S concentrations, was determined from the mean value of the titration of Black Sea water samples collected from the layer just above the anoxic zone at the depths of 15.8 – 16.0 isopycnal surfaces, rather than titrating iodine solution in distilled water.

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Two different mixed-reagent concentrations have been recommended for the SPM method[6] depending on the H_2S concentration in the sample water. Since, the use of high concentration mixed-reagent is suggested also for the analyses of samples with low sulfide concentration[6], ie., the use of higher concentration reagents does not affect the final results. Therefore, the same reagent concentrations (N,N-dimethyl-p-phenylendiamine – 4.0 g/l and $FeCl_3 \cdot 9H_2O$ – 6.0 g/l) were used for samples having less than 40 μM H_2S concentrations. The higher concentration reagents, recommended by Cline[6], was used only for the analysis of samples having more than 40 μM. Absorbance of the samples containing $[H_2S] > 40$ μM were determined after 10 times dilution with distilled water after the full development of color.

All volumetric flasks, used for both the sub-sampling of water and the preparation of sodium sulfide solutions in distilled water, were dried and flushed with oxygen free argon gas prior to their usage. Sub-sampling of water samples for SPM analysis were done by direct transfer of sulfidic water sample into the septum-sealed, argon gas containing, 50 ml capacity serum bottles having the mixed-reagent. The water sample transfer were done through a tygon tube having large cannula at one end. Argon gas in the serum bottle was driven through another smaller cannula. On the other hand, the sampling strategy was similar to that applied for the determination of dissolved oxygen. Water samples were transferred with the help of tygon tubing into 250 ml capacity volumetric flasks containing sufficient amount of iodine solution. Absorbance of the colored solu-

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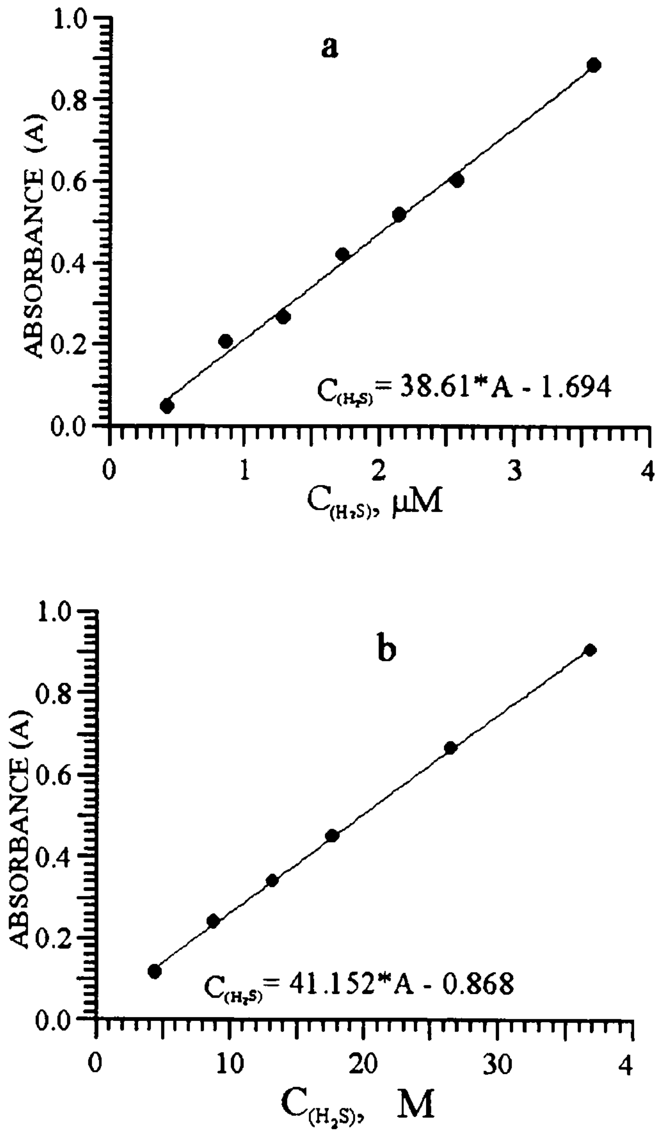

FIGURE 2 Calibration curves used in the SPM determination of hydrogen sulfide for two concentration ranges a) 0–4 μM, b) 0–40 μM ranges

tion, developed after 20 minutes, was measured by LKB Model spectrophotometer at λ=670 nm using a 50 mm quartz cell. Only freshly prepared solutions of sodium sulfide were used for making the calibration curves for the SPM method.

The exact concentration of the stock sulfide solution was determined by the IBT method as suggested by Cline[6]. Typical calibration curves used in the SPM measurements for different ranges of the sulfide concentration are displayed in Figure 2.

RESULTS AND DISCUSSION

Reproducibilities and precisions of the methods

The reproducibility of the IBT method has been estimated by analyzing the sea water samples collected from the same depth by a rosette type 12 Niskin samplers of 5 L capacity attached to SBE Model II CTD probe. Thus the data obtained through these experiments give not only the reproducibility of the analytical methods but also that of bottle sampling. Results of the reproducibility experiments for the SPM and IBT methods for both artificial sodium sulfide solutions and real sea water samples having 1–40 μM H_2S concentrations are given in Table I.

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Standard deviation of the IBT method was found to vary from 0.8 μM to 1.3 μM for 40 and 2 μM H_2S concentrations, respectively, whereas the average coefficient of variation which depends on the concentration of sulfide increases from 2.1% at 40 μM to 68% at 2 μM concentrations. On the other hand, the standard deviation of the SPM method varied from 0.11 μM to 1.4 μM for 2–40 μM range, and the average coefficient of variation varied from 6.8 % for less than 10 μM H_2S concentrations to 4.5% for higher concentration range. Statistical analysis of the data imply that SPM results are independent of the concentration and of the nature of the sample, i.e., natural or artificial samples.

Although the reproducibility of the SPM method is better for low hydrogen sulfide concentrations (<30 μM) which covers the water column down to 16.5 density surfaces, the IBT method gives more reliable results and convenient for higher concentrations, or for depths larger that 16.5 density surface.

Comparison of the results obtained by two methods

The results of H_2S analyses obtained by both IBT and SPM methods during the March, 1995 cruises of *R/V Bilim* (IMS) and of *R/V Professor Kolesnikov* (MHI), and the 1988 cruise of R/V *Knorr* are given in Table II for two different density surfaces in the anoxic layer. Comparison of the SPM results obtained during these different cruises in different years are in excellent agreement when they are compared in terms of the isopycnal surfaces rather than depth, and even though different sampling techniques were followed (pump-casting on R/V *Knorr*, and CTD attached Niskin type samplers on R/V *Bilim* and R/V *Professor Kolesnikov)* and the data sets are separated by 7-year interval.

TABLE I Reproducibility of hydrogen sulfide determinations by SPM and IBT methods for varying H_2S concentrations

Type of sample	*Method*	*Mean value, μM*	*Standard deviation σ_n, μM*	*Number of replicates*	*Coefficient of variation, %*
A	IBT	1.9	1.3	13	68.4
A	IBT	39	0.8	15	2.1
A	SPM	1.5	0.11	16	7.1
A	SPM	1.8	0.17	15	9.5
A	SPM	3.2	0.16	10	5.0
A	SPM	5.9	0.32	8	5.5
B	SPM	12.8	0.63	4	5.0
B	SPM	25.0	0.56	5	2.2
B	SPM	40.6	1.4	8	3.4
C	SPM	64.1	3.38	8	5.3
C	SPM	95.5	6.94	8	7.3

(A): Sea water; (B): Na_2S solution in distilled water; (C): Na_2S solution in sea water.

TABLE II Results of the hydrogen sulfide determinations by SPM and IBT methods at two selected density surfaces during different cruises (R/V Knorr-1988 data are taken from Friederich, et al.[22]

Density Surface σ_θ,	*Mean Value μM*	*σ_n*	*Replicates Number, n*	*C_{var}, %*
SPM Method				
R/V *Knorr*, June-July 1988				
16.30	8.4		1.8 21	21
16.50	30.0		2.1 21	7.0
R/V *Bilim*, March-April 1995				
16.30	9.4	0.9	12	9.4
16.50	28.7	2.5	10	8.7
R/V *Professor Kolesnikov*, March-April 1995				
16.30	8.5	1.4	17	17
16.50	28.5	1.6	12	5.7
IBT Method				
R/V *Professor Kolesnikov*, March-April 1995				
16.30	14.9	1.7	16	12
16.50	28.5	1.6	13	5.7

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However, the differences between the data sets from the same density surfaces become detectable when one compares the results of the SPM and IBT methods (Table II), even for the individual cruise-based data sets. Results obtained by both methods are in good agreement when the sulfide concentration is relatively high (28.5–30 μM at σ_t=16.5), but differences become significant when the concentration is low (8.4–16.1 μM at σ_t=16.3).

Based on this good correlation between these different data sets, basin-wide IBT and SPM data sets of of *R/V Bilim* and *R/V Professor Kolesnikov* were pooled to form a single data set, and plotted as a function of water density in Figure 3. As one can see from Figure 3, the mean concentration of hydrogen sulfide determined by the SPM method at any depth is always lower than that determined by the IBT method. In general, $[H_2S]_{IBT}$ / $[H_2S]_{SPM}$ ratio approaches to unity when sulfide concentration is higher than 30 μM level, and the difference between the IBT and SPM data is about 2% (Figure 4a). However, the difference could be as much as 10 – 30% between individual samples, and both methods could provide better results. The $[H_2S]_{IBT}$ / $[H_2S]_{SPM}$ ratio increases rapidly as the sulfide concentration decreases from 30 μM to about 10 μM (Figure 4b). Moreover, 3–5 μM H_2S concentration was always detected by the IBT in the anoxic interface, whereas SPM method gives undetectable levels for H_2S (<0.5 μM) for the same depths (see Figure 3). A similar conflict also arises in the data of Novosjolov et al.[13](see Figure 1).

The correlation between the results of SPM and IBT analyses (see Figure 4b) can be described by a second-order polynomial equation, with a coefficient of determination equal to 0.90, given below for the 0 – 30 μM sulfide concentration range.

$$Y = 0.027 \cdot X^2 + 0.238 \cdot X - 1.119,$$

where Y is $[H_2S]_{SPM}$ and x is $[H_2S]_{IBT}$.

The difference between the $[H_2S]_{IBT}$ and $[H_2S]_{SPM}$ is, on average, about 5–6 μM when $[H_2S]_{SPM}$ varies between 0 – 6 μM (see Figure 5), and becomes nearly zero when the $[H_2S]_{SPM}$ increases to 30 μM concentration. These remarks should be taken into account when the results obtained by SPM and IBT methods are to be used for the evaluation of long-term variations in the position of the hydrogen sulfide chemocline.

Interferences by oxidized forms of sulfur species

A good explanation for the discrepancies observed between these two methods can be found in the presence of sulfur containing species, such as SO_3^{2-}, $S_2O_3^{2-}$, S_n^{2-}, in the upper layer of the anoxic zone. However, the existence of such sulfur

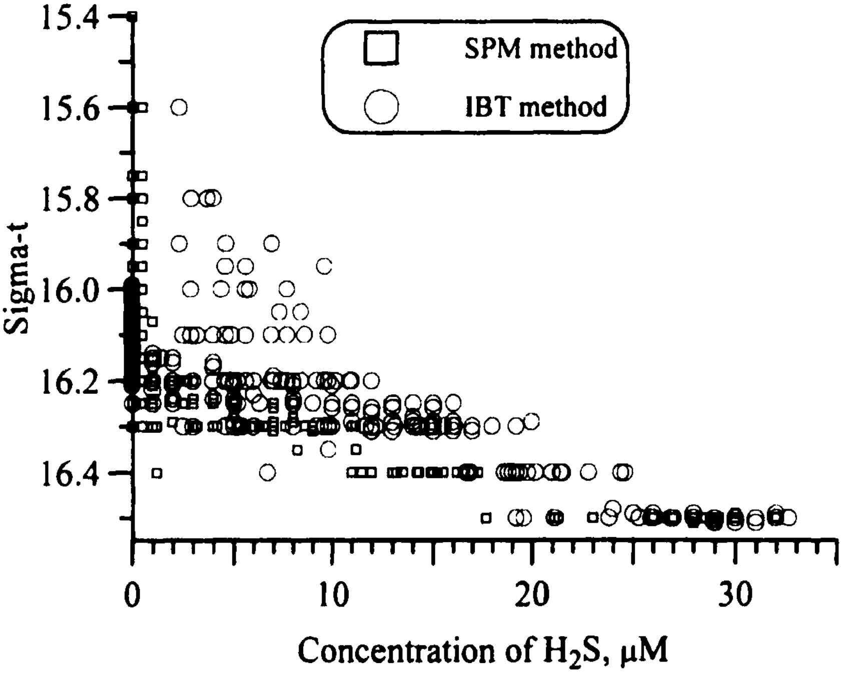

FIGURE 3 Water density dependent plots of H_2S concentrations obtained by SPM and IBT methods in the Black Sea

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species, except the elemental sulfur (S°), H_2S, $HS^-$and S^{2-}, is still debated[21]. Volkov et al.[10] insisted on the presence of hydrogen sulfide oxidation products at any depth in the anoxic zone of the Black Sea. This auhtor applied a series of complex chemical methods including precipitation, reduction and distillation for the determination of different sulfur species. Conversely, Luther et al.[7], by using voltammetric technique, have demonstrated quantitatively that certain sulfur species (SO_3^{2-}, $S_2O_3^{2-}$, S_x^{2-}) could only be detected if water samples from anoxic waters are exposed to aeration even for a short period. They found only $S_2O_3^{2-}$ when oxygen was allowed to enter the sampling bottle. Concentration of elemental sulfur was found to be less than 100 nM[21]. Studies of Yao and Millero[11] demonstrated that elemental sulfur (S°) is the dominant product of oxidation of H_2S both by Fe(III) hydroxides and MnO_2, whereas studies of Ciglenecki and Cosovic[12] have also shown the possibility of stabilisation of sulfur elements by organic matter and some metal sulfides in oxic waters within the fotic zone of the Adriatic Sea. All these sulfur reduced species, other than H_2S and its dissociation products, could consume iodine added to the samples in IBT, whereas they do not interfere in the interaction between sulfide and N,N-dimethyl-p-phenylendiamine in SPM.

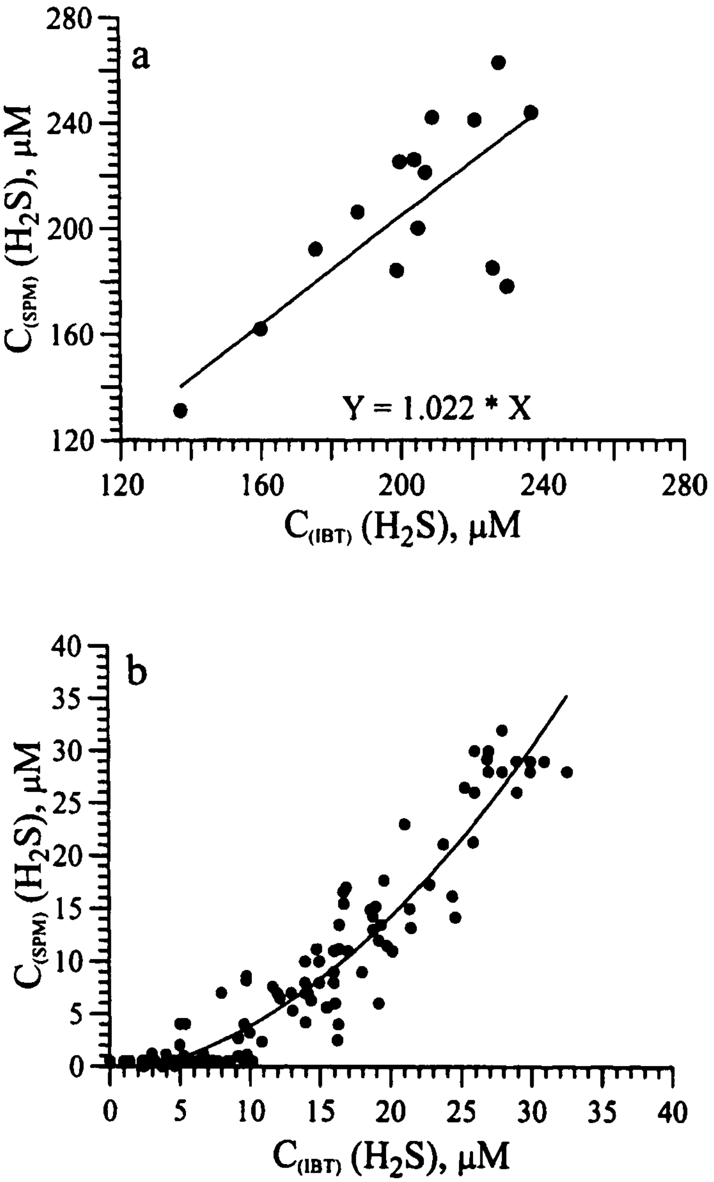

FIGURE 4 Plots of SPM data versus IBT data for the Black Sea. (a): for higher and (b): lower concentrations of H_2S

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Cline[6] pointed out that "thiosulfate and sulfite in the range of 0 – 100 μM do not prevent the full development of the color for SPM". However, we found that the absorbance of the colored solution obtained by mixing the solutions of 30 μM sodium sulfide and 30 μM sodium thiosulfate is 1.37 times lower than that of the 30 μM sodium sulfide solution alone. On the other hand, the absorbance of the 1:200 times diluted stock solution of Na_2S (~3000 μM) decreased from 0.40 to 0.17 after the storage of stock Na_2S solution in an amber colored bottle for 10 days at 25–28°C. This decrease in absorbance implies that the hydrogen sulfide concentration in the stock solution has decreased by about 2.4 times during storage. However, the results of IBT analysis for the same solution indicated that the concentration of the stored stock solution had decreased by only 4%.

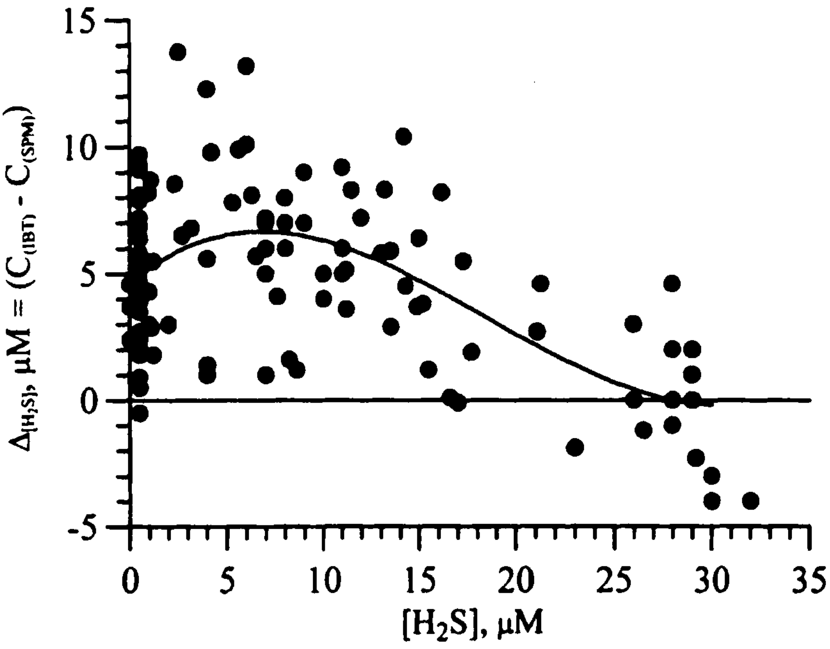

FIGURE 5 Plot of differences between IBT and SPM data versus H_2S concentration in the Black Sea

It is clearly evident that a newly prepared sodium sulfide solution has to be used for the preparation of calibration curves for the SPM method in order to avoid any interference from the oxidation products of sulfide, but the problems concerning the interference of hydrogen sulfide oxidation products on the results of the SPM analysis of real sea water samples still remain. Some additional studies (e.g. including voltammetry) are needed in order to clarify these uncertainties related to SPM determination of sulfide concentrations in the upper part of the Black Sea anoxic zone.

CONCLUSIONS

Even though the results obtained by the SPM and IBT methods are in good agreement for sea water samples having high H_2S concentrations (> 30 μM), reproducibility and precision of the SPM method are much better than that of the IBT for concentrations less than 30 μM, even when there is a clear difference between the mean values of these two methods. The average difference between these two methods, which is about 2%, can be as much as 10–30% for individual samples. Therefore, it is recommended to apply the SPM method for H_2S analyses in samples taken from the upper layer of the anoxic zone (i.e., [H2S]<30 μM) to determine the exact position of the sub-oxic zone boundaries.

Although the reason for this difference is not yet sufficiently clear, the most likely reason is the presence of some oxidation products of hydrogen sulfide (i.e. thiosulfate) both in the reagent solutions and in samples exposed to atmospheric oxygen.

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