

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

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Abstract. Iodometric Back Titration (IBT) and Spectrophotometric (SPM) determination are two commonly used methods for the determination of hydrogen sulfide (H_2S) concentration in sea water. These two methods were applied in parallel for analysis of Black Sea anoxic waters and artificial solutions containing different H_2S concentrations. The results of the SPM and IBT methods are in agreement when the H_2S concentration in sea water is higher than $30 \mu M$ and the precision of IBT is higher than that of SPM method. However, an opposite trend appears when the concentration of sulfide is less than $30 \mu M$; moreover, the SPM method provided lower results than the IBT values. This apparent difference is most probably due to the presence of some hydrogen sulfide oxidation products (e.g., thiosulfate) consuming the iodine solution added to samples, but the complexing agent (N,N-dimethyl-p-phenylendiamine) used in SPM method, reacts with H_2S only.

1. Introduction.

The determination of hydrogen sulfide is extremely important for any anoxic marine environment and it is one of the basic analyses for the Black sea where hydrogen sulfide appears at depths of 80 - 250 meters [1]. The answers to questions on the spatial and temporal variation of the oxic/anoxic transition zone depend, in particular, on the accuracy of hydrogen sulfide determination. There are three methods that are commonly applied for the determination of hydrogen sulfide in anoxic basins; namely, Iodometric Back Titration (IBT) [2,3], Spectrophotometric (SPM) determination [4,5,6], and Voltammetry [7].

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 non-selective, all other reduced sulfur species which reduce the iodine added to the sample will be also

measured as "hydrogen sulfide" [1,2,3]. Skopintsev [1] states that about 80% of all the iodine-reactive sulfur species are sulfide (S^{2-}) and hydrosulfide (HS^-). The undissociated form (H_2S) is less than 20% of the total hydrogen sulfide even at a depth of 2000 m. The remaining fraction of the reduced sulfur containing compounds is made up of thiosulfate ($S_2O_3^{2-}$), elemental sulfur (S^0), sulfite (SO_3^{2-}), polysulfides (S_n^{2-}), and poly-thionates [1,7,9]. Reduced forms of metals and organic matter also decrease the amount of iodine, but it is assumed that the concentration of these substances is very low in Black Sea waters. In general, the precision of IBT method is equal to 3% [8] except in the upper part of the anoxic zone where the concentration of hydrogen sulfide is less than $10 \mu M$.

Some investigators have used the SPM method for the determination of hydrogen sulfide in Black Sea waters due to its specificity in reaction and its high sensitivity [4,5,10,11,12]. It has been claimed that the SPM method is selective for hydrogen sulfide partitioned as H_2S , HS^- and S^{2-} in anoxic waters in the presence of other reduced forms of sulfur containing species [1,6,13]. The precision of this method for replicate sulfide analyses of artificial Na_2S solutions is $\pm 2\%$ at the 95% confidence level [6].

The SPM method is accepted as more convenient and sensitive than the IBT method. However, there exists an uncertainty when the results of the IBT and SPM methods are compared.

Gaines and Pilson [14] have announced a good agreement between the results obtained by both methods in an estuarine water where the total sulfide concentration was in the range of 160 to $4530 \mu M$. However, Lukashov [15] has stated that the SPM method is to be preferred when concentrations of hydrogen sulfide are less than 1 ml/l ($\sim 45 \mu M$). Interestingly, the H_2S concentrations measured by SPM method are relatively low as $H_2S > 50 \mu M$.

An opposite conclusion was reached by Bezborodov and Eremeev [16], by comparing the results obtained by different investigators in the anoxic waters of the Black Sea with $H_2S > 0.6-0.8$ ml/l ($27-36 \mu M$). There was an evident change in the slope of the vertical profiles of sulfide determined by using the spectrophotometric method. The vertical gradients of the sulfide concentration for SPM data were higher than that of the IBT profiles beginning from the above mentioned range concentration up to $50 \mu M$.

Novosjolov et al. [11] found no difference between the depths of the hydrogen sulfide onset when they used these two methods of analyzing the samples. After analyzing 57 samples from the upper part of the anoxic layer ($0 - 50 \mu M H_2S$) they reported that the results obtained by both methods were in good agreement, and the observed differences in the concentrations were attributed to the presence of thiosulfate [11]. However, when the data published by Novosjolov et al. [11] are replotted (Fig. 1), one can see the difference between the two methods. The slope of the $C_{(SPM)} - C_{(IBT)}$ regression is nearly 0.76 (Fig. 1), including the measurements with $H_2S > 5 \mu M$ only. It may be rather difficult to explain such a coherent difference in the slope by the presence of thiosulfate.

Since different investigators obtained contradictory results and conclusions, this

study has been conducted for the clarification of the indicated methodological problems and to form a basis for the comparison of results obtained by the IBT and SPM methods.

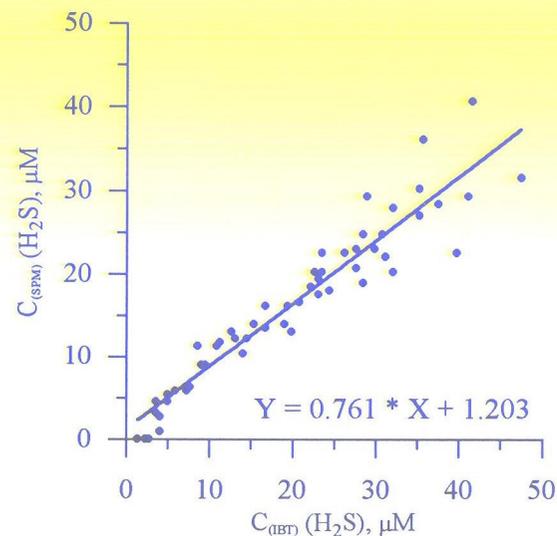


Figure 1. IBT method versus SPM method (Based on data from [11]).

2. Experimental section

The SPM [6] and IBT [17] methods were run in parallel for the analysis of H_2S during cruises in the Black Sea and under laboratory conditions. The iodine/thiosulfate ratio for the IBT method was determined from the mean value of the titration of water samples collected from the layer just above the anoxic zone from the isopycnal surfaces 15.8 -16.0.

Different concentrations of reagents are used in the SPM method [6], depending on the hydrogen sulfide concentration in the sample of water. However, the use of reagents at higher concentrations is possible for the analysis of samples with low hydrogen sulfide concentrations [6]. This leads to over consumption of reagents but does not affect the final results. The low concentrations of reagents (N,N-dimethyl-p-phenyldiamine - 4.0 g/l and $FeCl_3 \cdot 9H_2O$ - 6.0 g/l) were therefore used in this study if $H_2S < 40 \mu M$. The higher concentrations of reagents, recommended in [6], were used for the analysis of samples for $H_2S = 40-250 \mu M$. Thus, samples with $H_2S > 40 \mu M$ were diluted 10 times with distilled water after the development of colour.

All the glass flasks used both for the sampling of water and for the preparation of sodium sulfide solutions in distilled water were dried and flushed with oxygen free argon gas when the SPM method was applied. The sampling strategy was the same as for the determination of dissolved oxygen, thus, the sample bottle was overflowed by 1

- 1.5 volume of sample and reagents were added immediately after subsampling. The absorbency of colour developed after 20 minutes was measured at $\lambda=670$ nm using a 50 mm quartz cell. Only freshly prepared solutions of sodium sulfide were used for calibration of the SPM method. The exact sulfide concentration of the standard working solution was determined by the IBT method, as suggested by Cline [6].

Typical calibration curves obtained for different ranges of the sulfide concentration are displayed in Fig.2.

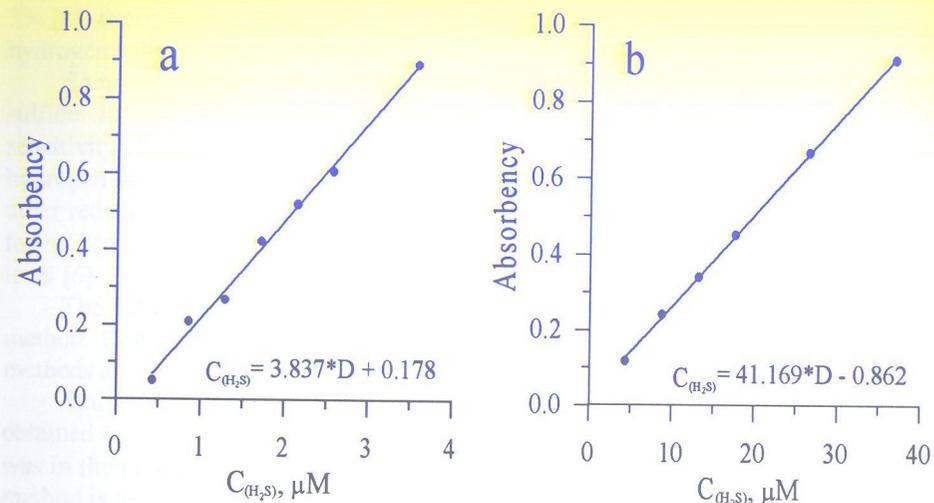


Figure 2. Calibration curves of the SPM method for different concentration ranges of sulfide. (a) For 0 - 4 μM
(b) For 0 - 40 μM

Different fit methods can be used to produce calibration curves. We used least square fit for linear approximation in this work.

3. Results and discussion

3.1 PRECISION OF THE METHODS

The reproducibility of the IBT method was estimated by analyzing sea water samples collected from the same depth by samplers attached to CTD probes. Thus the reproducibility of these results includes probable sampling errors as well as errors of the analytical procedure.

The reproducibility of the SPM method was determined by the analysis of both artificial sodium sulfide solutions and real sea water samples. In the case of the sea water analysis, each sample was drawn from a separate sampler. Replicates of artificial sulfide solutions were the standard working solutions of different sodium sulfide concentrations. Results are given in Table 1.

TABLE 1. Reproducibility of sulfide determination.

Type of sample	Method	Mean value, μM	Standard deviation, $\sigma_n, \mu\text{M}$	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 - Solution of Na_2S in distilled water; C - Solution of Na_2S in sea water.

The standard deviation of the IBT method, on the average, is equal to 1 μM . However, the coefficient of variation depends on the concentration of sulfide, increasing from 2% at 40 μM to 68% as the sulfide concentration being 2 μM . On the other hand, the coefficient of variation for the SPM method varies from 2.2 to 9.5% over the entire range of sulfide concentrations (1.5 - 95.5 μM). This value depends weakly on the concentration of sulfide or the nature of the sample (natural or artificial).

The reproducibility of the SPM method is much better than of the IBT when the concentration of hydrogen sulfide is less than 10 μM . On the contrary, the precision of the IBT method is better for high concentrations. Therefore, the SPM method is suggested to apply to samples from the upper anoxic zone of the Black Sea whilst the IBT method is more convenient for anoxic waters with high H_2S concentrations. However, the following two questions are still uncertain:

- Do the SPM and IBT methods produce comparable results?
- Does the SPM method measure H_2S selectively?

3.2 COMPARISON OF FIELD DATA

The results of the Black Sea water analysis of H_2S obtained by the IBT and SPM methods during the March-April, 1995 joint cruises of R/V *Bilim* (IMS) and R/V *Professor Kolesnikov* (MHI) and the 1988 cruise of R/V *Knorr* are given in Table 2.

The results obtained by the SPM method during different cruises in different

years are in excellent agreement although 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*) when the data are compared in terms of the isopycnal surfaces. However, the differences between the data sets from the same density surfaces become large when one compares the results of the SPM and IBT methods (Table 2) even for individual cruise-based data sets. Results obtained by both methods are in agreement when the sulfide concentration is relatively high ($\sigma_\theta=16.5$), but the differences become significant when the concentration is low ($\sigma_\theta=16.3$).

TABLE 2. Results of the sulfide determinations by SPM and IBT at depths of the selected density surfaces

σ_θ , sigma- θ	mean value μM	σ_n	n replicates	C_{var} , %
SPM method				
RV <i>Knorr</i> , June-July 1988				
16.30	8.4	1.8	21	21
16.50	30.0	2.1	21	7.0
RV <i>Bilim</i> , March-April 1995				
16.30	9.4	0.9	12	9.4
16.50	28.7	2.5	10	8.7
RV <i>Professor Kolesnikov</i> , March-April 1995				
16.30	8.5	1.4	17	17
16.50	28.5	1.6	12	5.7
IBT method				
RV <i>Professor Kolesnikov</i> , March-April 1995				
16.30	14.9	1.7	16	12
16.50	28.5	1.6	13	5.7

Based on the above mentioned consistency between the results of SPM method, we compiled the data sets of R/V *Bilim* and R/V *Professor Kolesnikov* obtained in 1995 for the comparison of SPM and IBT methods (see Fig.3). As one can see, the mean concentration of sulfide determined by the SPM method at any depth is always less than or equal to the value determined by the IBT method. In a general sense, the $C_{\text{IBT}}(\text{H}_2\text{S})/C_{\text{SPM}}(\text{H}_2\text{S})$ ratio is close to unity when the sulfide concentration is higher than $30 \mu\text{M}$ (Fig.4a). The difference between the results of the IBT and the SPM analyses is about 2% (Fig.4a). However, this difference could be as much as 10 - 30% between individual samples and both methods could provide higher results.

The $C_{\text{IBT}}(\text{H}_2\text{S})/C_{\text{SPM}}(\text{H}_2\text{S})$ ratio increases quickly as the sulfide concentrations decrease from $30 \mu\text{M}$ to about $9 \mu\text{M}$ (Fig.4b). Moreover, at the anoxic interface the H_2S concentration of $3 - 5 \mu\text{M}$ was always detected by the IBT whereas the SPM method measured undetectable levels of H_2S ($<1.0 \mu\text{M}$) at the same depths (Fig.3). The same conflict also arises in the data of Novosjolov et al. [11] (Fig.1). The correlation between the results of the SPM and the IBT methods can be described by the equation

given below for sulfide concentrations ranging from 0 to $30 \mu\text{M}$.

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

where Y is $C_{\text{SPM}}(\text{H}_2\text{S})$, X is $C_{\text{IBT}}(\text{H}_2\text{S})$, and the coefficient of determination is equal

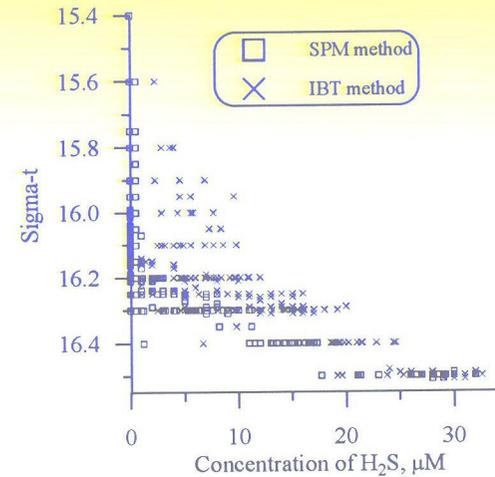


Figure 3. IBT and SPM methods versus density.

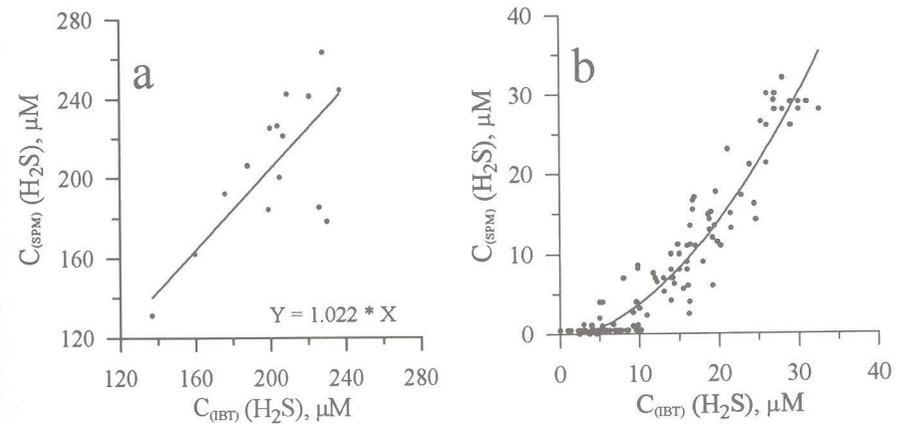


Figure 4. IBT method versus SPM method for different ranges of the sulfide concentration. (a) For 120-240 μM . (b) For 0-35 μM

to 0.90. On average, the difference $C_{\text{IBT}}(\text{H}_2\text{S}) - C_{\text{SPM}}(\text{H}_2\text{S})$ is equal to $5-6 \mu\text{M}$ when $C_{\text{SPM}}(\text{H}_2\text{S})$ lies between 0 and $16 \mu\text{M}$ (Fig.5) and it becomes close to zero when the

$C_{(SPM)}(H_2S)$ value increases from 16 μM to about 30 μM . These points should be taken into account when the results obtained by the SPM and IBT methods and the long-term changes in the position of the hydrogen sulfide onset are discussed.

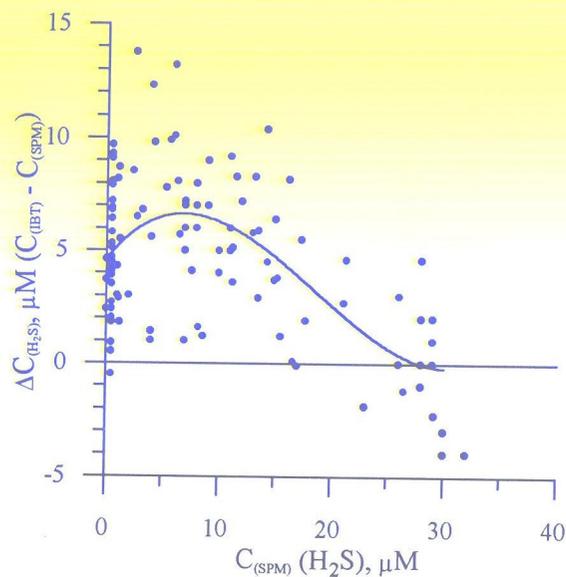


Figure 5. Difference between the results of the IBT and the SPM methods as a function of the sulfide concentration in sea water.

It seems most logical to explain the discrepancy between the two methods as being due to 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 and concentration of such sulfur species, other than elemental sulfur (S^0), hydrogen sulfide (H_2S), and its dissociation products (HS^- , S^{2-}), are still debated. Volkov [9] insists on the presence of hydrogen sulfide oxidation products at any depth in the anoxic zone of the Black Sea, while Luther [7] argues against it. Volkov et al. [18] applied complex chemical methods, including precipitation, reduction and distillation for the determination of different sulfur species, whereas Luther [7] used voltammetry, determining quantitatively certain sulfur species, (including S^0 , H_2S , HS^- , and S^{2-}). The concentrations of these ions (SO_3^{2-} , $S_2O_3^{2-}$, S_n^{2-}) are negligible if atmospheric contamination of the samples is prevented [7]. In any case, the data obtained during the present study and those of Volkov [9] and Luther [7] contradict each other. Therefore we would suggest SO_3^{2-} , $S_2O_3^{2-}$, S_n^{2-} or some other forms of sulfur to be present in the most upper part of the anoxic layer only and to be at trace levels in the deep anoxic waters of the Black Sea.

On the other hand, we can suppose that some sulfur compounds (e.g., SO_3^{2-} , $S_2O_3^{2-}$, S_n^{2-}) could interfere in the interaction between sulfide and N,N-dimethyl-p-phenylendiamine, as discussed briefly below.

3.3 INTERFERENCE OF SULFUR CONTAINED SUBSTANCES

Cline [6] has pointed out that "thiosulfate and sulfite (up to 100 μM) do not prevent the full development of the color". However, we found that the absorbency was reduced by 37% when a mixture of 30 μM of sodium sulfide and 30 μM of sodium thiosulfate was analyzed as compared to that of 30 μM sodium sulfide solution alone. On the other hand, the absorbency of the 200 times diluted solution of Na_2S decreased from 0.40 to 0.17 when the stock solution of $\sim 3000 \mu M$ was kept in an amber coloured bottle for 10 days at 25-28°C. The decrease in absorbency implies that the sulfide concentration has decreased 2.35 times during the storage. However, the results of IBT analysis for the same solution indicated that the concentration decreased only by 4%.

It is clear that a newly prepared sodium sulfide standard must be used for the preparation of calibration curves in order to avoid any interference from the oxidation products of sulfide and loss of H_2S in the solution. However, the problems concerning the interference of other sulfide species in H_2S analysis by SPM method in sea water samples still remain unresolved.

4. Conclusions

Sulfide data obtained by different groups, who followed the SPM method in sea water analysis are very consistent when the data sets are compared relative to water density. However, the results from the SPM and IBT methods are in agreement provided that the concentration of sulfide in sea water is higher than 30 μM . The precision of IBT method is much better than that of SPM as $H_2S > 30-40 \mu M$ whereas, the reproducibility of SPM method is much better than that of the IBT for concentration of H_2S less than 40 μM . It is recommended to apply the SPM method for sulfide analysis of waters from the anoxic interface ($H_2S < 30 \mu M$). The sulfide concentration obtained by the two methods displayed remarkable difference in the interface having lower H_2S with the SPM. Unfortunately, the reason for this coherent difference is still unclear; but the most possible factor is the presence of some other sulfur containing compounds (i.e. thiosulfate) which react with the iodine added to the sample, but do not react with N,N-dimethyl-p-phenylendiamine.

5. Acknowledgments

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SOME REMARKS SUBOXIC ZONE

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Abstract. This work reports on the oxidation rates of hydrogen sulfide in the Black Sea. The measured rate constants ($\sigma_0 = 15.70-16.20$) are compared with those of H_2S removal measured in the river. The largest half-lives were displayed by minimum distributions of particulate Mn were also detected. Particulate forms of Mn were also detected filtered through 1.2

1. Introduction

Whenever the rate of consumption rate of hydrogen sulfide distribution of manganese reducing condition catalytic actions of oxidation of sinking

(CH_2O)

Oxic/anoxic boundary in the Black Sea have been studied. The chemistry and the speciation of manganese that may occur in