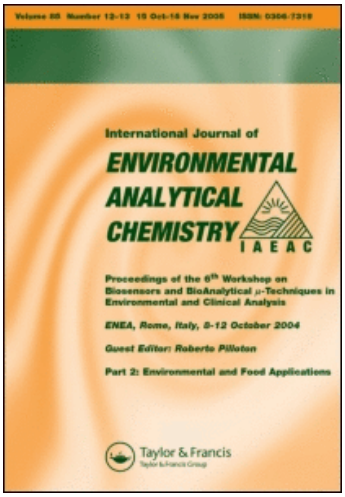

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Pneumatoamperometric Determination of Sulfur Dioxide in Air on ppb Level

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A simple device for the determination of sulfur dioxide at ppb concentrations in air is described. The device is composed of an enrichment unit operating continuously on the basis of gas extraction into polydisperse aerosol of a liquid transferring sulfur dioxide from liter amount of air into microliter amount of liquid. The analyte is determined pneumatoamperically from the concentrate on a gold-plated porous Teflon electrode.

The detection limit is 0.3 ppb (v), i.e. 0.87 $\mu g/m^3$ of sulfur dioxide, the linear range covers several orders of magnitude. The analytical response is obtained few tenths of seconds after the gas contaminated with sulfur dioxide has entered the enrichment unit.

KEY WORDS: Determination of sulfur dioxide in air, trace analysis, enrichment unit, pneumatoamperometry.

INTRODUCTION

Pneumatoamperometry (the name introduced by Gifford and Bruckenstein[1]) is a sensitive analytical method, by means of which the dissolved analyte reacts with a suitable reagent to produce an equivalent amount of a volatile electrochemically active compound. The compound is transferred into the carrier gas stream and determined amperometrically on a membrane electrode. The survey of applications can be found elsewhere.[2]

Pneumatoamperometric analysis proceeds in two ways: either the reagent is added into the analyzed solution or solution of the analyte is introduced into the solution of the reagent. The latter procedure is faster. In view of small volumes of samples that are usually introduced (10–100 μl) a 10^{-6}–10^{-5} molar concentration of analyte is necessary in the sample. This concentration relates to the amount of units up to tenths of nanogrammes of the analyte in the sample. Such amounts are for pneumatoamperometric determination optimal.

Trace compounds from air (gaseous media) can be obtained in solutions at sufficient concentrations by their accumulation in an absorption solution. Common procedures for the concentration using gas bubbling through the absorption solution are for amperometry not effective. Large volumes of liquid must be used (ca. 10 ml) making the absorption time excessively long.

Pneumatoamperometric determination of sulfites has been described by Nygaard[3]. He used an electrode of compact platinum with an electrolyte film (1 M H_2SO_4), coated with a nonporous polyethylene membrane. This arrangement provides low sensitivity (9×10^{-5} nA/ng SO_2), relatively high value of the detection limit (100 ng/ml SO_2) and requires a long response time (650 s).

In the present paper we applied a special enrichment technique[4] based on the principle of equilibrium accumulation of substances from gas by polydisperse liquid aerosol and making it possible to transfer traces of the analyte from large volumes (10^3 ml) into a small volume of the liquid (10^{-2} ml). Exceptionally high degree of enrichment of gaseous analyte makes pneumatoamperometric detection easy. The analyte, sulfur dioxide, was sorbed in the enrichment unit in both water and the solution of sodium mercuro(II)tetrachloride. It was liberated from the solution by an acid and determined amperometrically with a gold-plated porous Teflon electrode.

TABLE I

Results of sulfur dioxide sorption by water

Date	Condensate flow rate u_L μl/s	Sorption efficiency %	Room temperature K
10.4.	5.8	65.4	
24.4.	3.0	60.7	298.4
	16.4	63.5	
25.4.	16.74	64.6	298.3
14.5.	2.33	65.4	300.3
10.7.	3.15	63.5	297.7
	6.59	68.2	
	10.97	63.3	
	15.37	65.0	
	20.67	66.5	

TABLE II

Results of sorption by phosphate buffer (0.05 M $KH_2PO_4 + Na_2HPO_4$), flow rate $u_L = 3.1$ μl/s

pH	Sorption efficiency %
5.89	61.2
6.39	67.9
7.35	63.8
8.17	65.4

range studied u_G/u_L (see Table I). Within the studied range of pH, i.e., 5.89 to 8.17 (phosphate buffer 0.05 M $KH_2PO_4 + Na_2HPO_4$), the sorption efficiency does not evidently depend on pH value (Table II). Under these conditions, sulfur dioxide is present in the solution as HSO_3^- and SO_3^{2-} species.[6]

The stability of sulfur dioxide concentrate was investigated for samples containing 1 μg/ml of sulfur dioxide for the period of 24 hours. It was found that the decrease in the sulfur dioxide content in the concentrate was about 20% after 24 hours for the samples kept in the light at room temperature whereas the decrease for the

K_1, K_2 are the dissociation constants of $SO_2 . H_2O$ into the first and the second degrees, respectively;

$[H^+]$ is the equilibrium concentration of hydrogen ions in the concentrate.

If sodium mercuro(II)tetrachloride solution is used as the sorption medium, then it applies to the total molar concentration of tetradentate sulfur in the concentrate

$$[S^{IV}] = [SO_2 . H_2O] + [HSO_3^-] + [SO_3^{2-}] + [[HgCl_2SO_3]^{2-}],$$

and the following relationship is valid for the distribution constant

$$K_{iL} = \frac{[S^{IV}]}{[SO_2]_G} = K_H + \frac{K_1 . K_H}{[H^+]} + \frac{K_1 K_2 K_H}{[H^+]^2} + \frac{K_3 K_H [Na_2HgCl_4]}{[H^+]^2 . [Cl^-]^2} \quad (3)$$

where K_3 designates the equilibrium constant of the complex-forming reaction of sulfur dioxide with sodium mercuro(II)tetrachloride.

EXPERIMENTAL

Diagram of the assembly

The method has been tested with the apparatus whose diagram is in Figure 1. Air is sucked by a vacuum pump through a filter (1) with sodium hydroxide that captures atmospheric sulfur dioxide. Pure air is enriched with sulfur dioxide traces in a defined way. It masses above a thermostated vessel containing sulfur dioxide, closed with a permeation disk. At 323 *K* the permeation disk produced 4.2 ng/s of sulfur dioxide. To avoid the cooling of the disk by the air stream, only a small volume of air (ca. 3 ml/s), split by a pneumatic resistance of a restricting capillary (2), passed through a permeation cell (3). The total air volume entering an enrichment unit (6) is given by the diameter of the nebulizer inlet jet and the underpressure in the enrichment unit. The measurements were performed at an

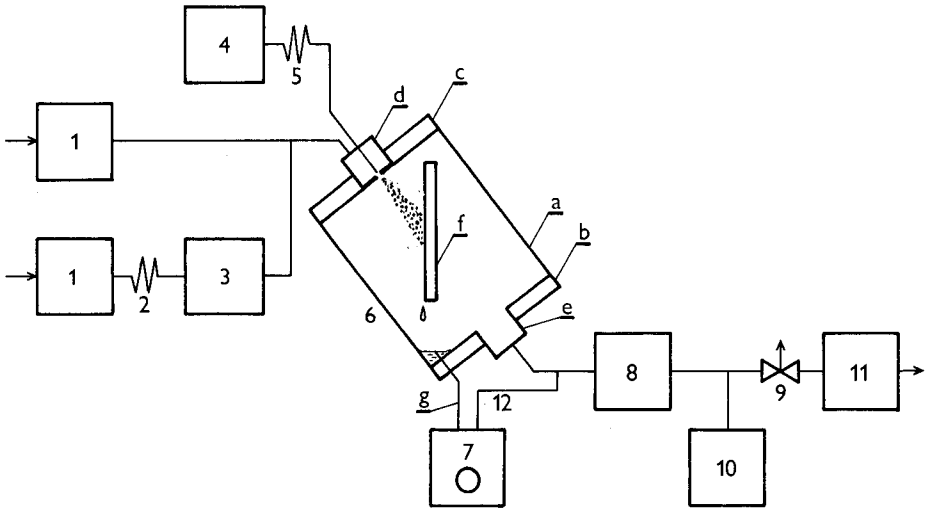

FIGURE 1 Diagram of apparatus: (1) filter with NaOH, (2, 5) restricting capillaries, (3) SO_2 source, (4) absorption liquid reservoir, (6) enrichment unit (for detailed description see text), (7) sample collector, (8) flowmeter, (9) valve, (10) manometer, (11) vacuum pump, (12) tubing permitting spontaneous sample flow from the enrichment unit (ensuring slight underpressure in container 7 in comparison with the pressure in the enrichment unit).

underpressure of 40 kPa which was set by a valve (9) and measured with a mercury manometer (10). With a given nebulizer construction, volume flow rate of the sucked air was $u_G = 72$ ml/s. This volume flow rate was maintained at the same value in all our measurements. With the above mentioned volume flow rate and production of sulfur dioxide, the air entering the nebulizer contained 0.058 mg/m^3 of sulfur dioxide (20 ppb (v)). The ratio of the gas flow rate to the sorption medium flow rate, u_G/u_L, was controlled by the change in the flow rate of the liquid entering the nebulizer from a reservoir (4). The flow rate was set by the change in the length of a restricting capillary (5). The sorption efficiency was tested for the u_G/u_L ratios in the range 3.48×10^3–3.09×10^4, for the flow rates of the liquid ranging from 2.33 to 20.67 μl/s. The flow rate was measured at the enrichment unit outlet. The concentrate flows into a collecting zone (7) from where it was taken for analysis with a microliter syringe through a rubber septum.

Enrichment unit

Schematic diagram is also given in Figure 1. It is a silanized glass cylinder (6a) with internal dimensions: length of 100 mm, diameter of 45 mm. The cylinder is closed with Teflon faces (6b, c). Nebulizer (6d) is screwed in the inlet face. Ejection effects of the sucked air streaming at a linear velocity of ca. 150 m/s form a polydisperse liquid aerosol. The analyte contaminating the air is sorbed on aerosol particles. The outlet face is equipped with a passage (6e) by which the enrichment unit is attached to a source of vacuum (11). A barrier (6f) is placed inside the unit, inclined 30° from the longitudinal cylinder axis. After quasi adiabatic air expansion and due to impact, the aerosol coagulates on the barrier, the concentrate flows down into a collecting zone and flows out via a tube (6g).

Pneumatoamperometric apparatus

The apparatus described by Gifford and Bruckenstein[1] was used to analyze the analyte. The procedure for the preparation of metal-plated Teflon membrane electrode (AuPME) is also presented there. We prepared the membrane by vacuum evaporation of gold on a Gore-Tex No. S10363 porous polytetrafluoroethylene membrane (W. L. Gore and Associates, Inc., Elkton, MD, USA). The surface area of the electroactive electrode section was ca. 40 mm^2. The AuPME was immersed in 0.1 M K_2SO_4 solution and SO_2 was determined by oxidation at +0.6 V/SCE. Nitrogen was used as a carrier gas at a volume flow rate of 8 ml/s. The AuPME was stored dry in the air overnight. Prior to measurement, electrochemical activation by a two-fold polarization between +1.5 and −1.5 V/SCE proved good. After the activation, the residual current settled at a constant value within ca. 30 minutes. The reaction vessel was filled with 2 ml of 6 M H_2SO_4 and 20 μl of the concentrate were injected into it in all the measurements.

Chemicals

All the chemicals used were prepared of A.R. grade chemicals. The stock solution of 0.1 M sodium mercuro(II)tetrachloride (TCM) was prepared by dissolving 27.2 g $HgCl_2$ and 11.7 g NaCl in one liter of

distilled water. The stock solution of sodium hydrogensulfite was prepared by dissolving $NaHSO_3$ in 10^{-2} M TCM to give the solution containing 100 μg/ml of SO_2. The solution was prepared fresh daily. Sulfur dioxide content used in sodium hydrogensulfite was determined by iodometric titration. Standard solutions were prepared by diluting the stock solution of 10^{-2} M TCM. Water was re-distilled in a quartz apparatus. The measurements were carried out at room temperature, i.e. at 293 ∓ 2 K.

RESULTS

Calibration

The dependence of AuPME response (peak height I_p) on the amount of sulfur dioxide is linear over the range from 3 to 120 ng. For the set of ten samples from this range, the parameters of regression equation are $I_p(\text{nA}) = (31.8 \pm 0.9)$ ng $SO_2 - (1.1 \pm 5.8)$ with the standard error of 4.1 nA and the correlation coefficient of 0.9997.

The relative standard deviation for 30 ng SO_2, determined from the set of eleven measurements, was 1.4%. The detection limit c_L = (three times the standard error)/(regression straight line slope) is 19 ng SO_2 in 1 ml of the solution. The AuPME signal expires in about 100 s. The noise of the residual current did not exceed 3 nA.

The above results are valid for sulfur dioxide oxidation in 0.1 M K_2SO_4. In sulfuric acid, used most frequently as an electrolyte in SO_2 oxidation (see, e.g., refs. 3, 5). the response is lower and decreases with the increasing acid concentration. In 0.1 M H_2SO_4, it was approximately 10 times lower than the response in 0.1 M K_2SO_4.

6 M H_2SO_4 was used to evolve SO_2 from the sample solution. Thereby foaming was avoided and evaporation was suppressed in comparison with more dilute solutions. Sulfur dioxide is emitted even at sulfuric acid concentrations lower by one order of magnitude. It was also found that sulfur dioxide is emitted at an identical rate from both aqueous and TCM solution.

Sulfur dioxide sorption by water

When water was used as a sorption medium in the enrichment unit, the sorption efficiency of $64.6 \mp 1.5\%$ was found within the entire

samples kept in the dark was 4%. It is therefore more suitable to perform absorption and store the concentrate from the enrichment unit in the dark. To investigate the influence of heavy metal traces that catalyze dulfur dioxide oxidation, the samples were also tested in 10^{-4} M Chelaton III (disodium ethylenediaminetetraacetate). Oxidation to the inactive form (SO_4^{2-}) is negligible. If the concentrate is subjected to the analysis within two to three hours after being taken from the enrichment unit, the error of the determination due to sulfur dioxide loss is negligible.

Respecting the detection limit of the pneumatoamperometric method of ca. 19 ng of sulfur dioxide in 1 ml of the absorption liquid, the efficiency of absorption by water is 65% for the ratio $u_G/u_L = 3.09 \times 10^4$. The detection limit of sulfur dioxide determination in air is 8×10^{-4} mg/m^3 (0.3 ppb by vol). At a liquid flow rate of 2 μl/s, the concentrate is theoretically at disposal 10 s after the air contaminated with sulfur dioxide passed through the enrichment unit.

Sulfur dioxide sorption by TCM

Sulfur dioxide is bonded in TCM solution in the form of a stable complex $(Hg(SO_3)_2)^{2-}$. This complex is stable to such an extent that it suppresses reversible evolution of sulfur dioxide from the concentrate into the gas phase. Hence an increased sorption efficiency can be expected. This assumption is in accord with the experiment (Table III). Sorption by TCM is complicated by reduction of TCM which is converted to calomel. In currently used solutions, i.e., in 0.1 M TCM and at the concentrations above 1 mg/ml of sulfur dioxide, TCM reduction proceeds slowly.[7] Under the conditions of atmospheric sulfur dioxide sorption by TCM, calomel is produced in the enrichment unit at sulfur dioxide concentrations lower by one order of magnitude. TCM reduction manifests itself in the decrease in the absorption efficiency. As the content of sulfur dioxide in the concentrate rises, calomel is formed and its deposition on the walls of the enrichment unit is noticeable. The reduction can be suppressed by using more dilute solutions of TCM (see Table III).

When very strongly dilute TCM solutions are used, however, problems arise associated with the stability of bonded sulfur dioxide caused by increased ionization of mercuro(II)tetrachloro-complex.[8] Figure 2 illustrates graphically the results of the study on sulfur

TABLE III

Results of sulfur dioxide sorption by TCM solution

flow rate u_L μl/s	3.1	6.8	11.4
TCM concentration in M	sorption efficiency %		
10^{-1}	[a]	[a]	[a]
10^{-2}	[a]	[a]	90[c](0.3)[b]
5.10^{-3}	[a]	97[c](0.6)[b]	99.3
10^{-3}	94[c](1.3)[b]	100.8	103.2
10^{-4}	100.7	101.0	99.8

[a]Sulfur dioxide cannot be determined, it forms calomel noticeably.
[b]The observed sulfur dioxide concentration in concentrate in μg/ml.
[c]Sorption efficiency decreases with time; given values were found ca. 60 minutes after sorption in enrichment unit.

dioxide stability in 10^{-4} M TCM under various experimental conditions. Pure 10^{-4} M TCM solution can only be used provided that sulfur dioxide determination is performed straight after its absorption. Favourable influence of Chelaton III manifested itself in a buffered solution in which no difference in the sulfur dioxide content was found for the samples stored in the dark and for those stored in the light.

It is obvious from the results that water is a more advantageous sorption medium since the increase in the sorption efficiency of TCM is not so marked as to balance the above mentioned complications.

DISCUSSION

Various values of the distribution constant (K_{iL}) are obtained by solving Eq. (2) for the sorption of 20 ppb (v) of sulfur dioxide from 72 ml/s of air by water in the range from 2.33 μl/s to 20.67 μl/s of the sorption medium. The value is 1.418×10^4 for the former value and 1.412×10^5 for the latter one if the values of $K_H = 27.06$, $K_1 = 1.65 \times 10^{-2}$ mol/l and $K_2 = 6.51 \times 10^{-8}$ mol/l, calculated for 298 K on the basis of the data published by Walcek and Pruppacher,[9] are

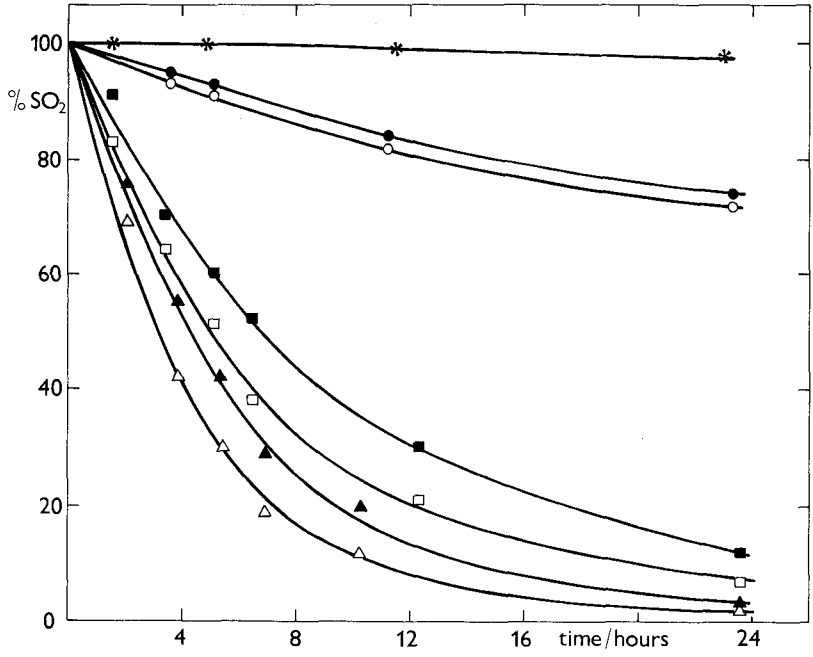

FIGURE 2 SO_2 loss with time in the solution of 10^{-4} M TCM under various experimental conditions. SO_2 concentration: 1 μg/ml, black points—sample stored in the dark, white points—sample kept in the light. △ 10^{-4} M TCM at pH 5.09. □ 10^{-4} M TCM + 10^{-4} M Chelaton III at pH 4.0. ○ 10^{-4} M TCM in phosphate buffer, pH 6.95. * 10^{-4} M TCM + 10^{-4} M Chelaton III in buffer, pH 6.95.

taken into consideration in the calculation. The dissociation of hydrated sulfur dioxide to the first degree, i.e., to hydrogensulfite (HSO_3^-) whose occurrence is higher than 98%, has the major effect on the value of this constant. By solving relationship (1) numerically, values of Q_{iL}/Q_{iG} are obtained for the above mentioned K_{iL} that differ markedly from experimentally found value $Q_{iL}/Q_{iG} = 0.645$. The enrichment unit efficiency determined experimentally is independent of water flow rate through the enrichment unit in the range from 2.33–20.67 μl/s (cf. Table I). Analogously, neither did the change in pH affect the value of this ratio (cf. Table II).

This contradiction can be ascribed neither to the change in the sulfur dioxide concentration gradient between the gas and liquid phases (viz. relatively wide range of the change in the volume flow

rate of water through the enrichment unit) nor to the loss of the tetradentate sulfur from the liquid phase due to the possible oxidation to sulfate anion (proven experimentally). Similarly as in the case of slightly volatile analytes in air,[4] it appears that the mechanism controlling sorption is more likely adsorption on a large surface of water aerodispersion rather than the dissolution proper. Therefore it seems that the difference between theory and experiment observed for sulfur dioxide should be ascribed to a comparable rate of two processes: mass transfer of the sulfur dioxide adsorbed on the surface of aerosol droplets into the gas phase and HSO_3^- formation in the water solution from $SO_2.H_2O$ originated during adsorption of SO_2 on the water surface. This is also supported by the results of sulfur dioxide determination after its absorption by sodium mercuro-(II)tetrachloride in which the reversible reaction is markedly suppressed.

The observed facts are favourable from the viewpoint of the determination of sulfur dioxide trace concentrations in the atmosphere. They suggest that neither quantitative analyte absorption nor solution buffering to a constant pH value are necessary in order to obtain reliable results.

When water is used as a sorption medium a conversion factor 1.548 was used to obtain analytical quantity Q_{iG}.

CONCLUSION

Sorption by water (or another sorption medium) of sulfur dioxide from air involving the enrichment unit coupled with the pneumatoamperometric assessment makes it possible to determine trace amounts of sulfur dioxide in the atmosphere. The determined detection limit of 0.3ppb (v) is by an order of magnitude better than the detection limit reported by other authors[10] who used for sulfur dioxide determination in air the enrichment by dispersion of the solution of flavin mononucleotide with a subsequent chemiluminescence analysis of the concentrate.

The pneumatoamperometric determination does not require any special apparatus and sensing elements and it generates a linear response to sulfur dioxide concentration within the range of several orders of magnitude. The necessity of periodic sampling of the

concentrate is a certain drawback of the above described arrangement.

Hydrogen sulfide and nitrogen oxides are the compounds interfering with the pneumatoamperometric sulfur dioxide determination in air. Interference due to nitrogen oxides can be eliminated by adding amidosulphonic acid to the adsorption solution prior to the analysis. Hydrogen sulfide occurs in the atmosphere at concentrations lower by one order of magnitude than sulfur dioxide does. Should hydrogen sulfide interfere significantly, TCM solution must be used as an absorption medium and the precipitate of HgS must be removed prior to the analysis.

Sulfur dioxide content in the concentrate from the enrichment unit can evidently be determined also by other analytical methods. The methods can, owing to a high degree of accumulation, be even less sensitive and permit even continuous monitoring. A combination of the enrichment unit with FIA instrumentation may be of interest.

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