DETERMINATION OF SUBNANOGRAM AMOUNTS OF SULFUR DIOXIDE AND SULFITES BY PNEUMATOPOTENTIOMETRY

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Gold porous membrane electrode has been used for the potentiometric determination of small amounts of sulfur dioxide absorbed in the solutions of sodium tetrachloromercurate or sodium hydroxide. Sulfur dioxide is released by the reaction with an acid into a stream of nitrogen and led to the electrode immersed into the solution of iodine monochloride. Part of SO_2 penetrates through the membrane pores into the solution where it is oxidized. The electrode redox potential change is a measure of the SO_2 concentration in the absorption solution. In the solution of $1 . 10^{-5}M [ICl_2]^-$ in $0·02M\text{-}HClO_4$ the limit of quantitation was found to be $0·07$ ng $SO_2 . ml^{-1}$. The relative standard deviations of $1·4\%$ and $2·5\%$ were found for the determinations of 10 ng and 0·5 ng of SO_2, respectively. Higher concentrations of H_2S interfere only in the hydroxide solution. About 10 samples can be analyzed per one hour.

Sulfur dioxide is one of the most frequently analyzed gases contributing to the atmospheric pollution. Its concentration exceeds usually the concentrations of other common pollutants so that it is considered as an indicator of the pollution degree.

SO_2 can be determined by many methods and analyzers surveyed in monographs and reviews, *e.g.*,[1-3]. However, the most common method is the photometric method by West and Gaeke[4] that is considered as a standard method of SO_2 determination in atmosphere. Its principle is based on the absorption of SO_2 in the sodium tetrachloromercurate solution. The compound formed reacts with pararosaniline and formaldehyde giving a red-violet product. The coloration intensity is used as the measure of SO_2 concentration in the absorption solution. The detection limit was determined to about 50 ng of SO_2 in 1 ml of the absorption solution (*i.e.*, about 50 ppb). The dependence of the coloration on the quality of pararosaniline is the main problem of this method so that many modifications of the original procedure were proposed (*cf.*[5] and references therein) with no substantial improvement achieved.

In this study the very sensitive pneumatopotentiometric method, used recently for the determination of cyanides[6], is adopted for the determination of SO_2 absorbed in the absorption solution. Sulfur dioxide is released from a given volume of the absorption solution by a reaction with an acid, transferred by bubbling into a stream of a carrier gas and led to the gold porous membrane electrode (AuPME). The electrode is immersed in the oxidizing agent solution $[ICl_2]^-$ and its redox potential

is measured. Part of SO_2 from the carrier gas diffuses through the membrane pores into the solution where oxidation takes place. The change of the agent composition in the vicinity of AuPME is reflected by the change of the redox potential and it is a measure of the SO_2 content in the carrier gas and therefore also in the absorption solution. This procedure eliminates the shortcomings of the photometric determination, particularly the effect of the agent quality changes, reduces the time required for the coloration development, avoids the problems with the colour stability and, last but not least, it makes possible to achieve higher sensitivity of the determination so that the period of SO_2 absorption from the analyzed medium into the absorption solution can be reduced.

In contrast to the classical equilibrium potentiometry the ratio $[ICl_2]^-/I_2$ in pneumatopotentiometry is not changed throughout the bulk of the solution but only in the immediate vicinity of the indication electrode. This change is counteracted by diffusion transport processes. In the moment of the SO_2 flow interruption from the analyzed sample, these processes reestablish the initial state at the surface of the electrode as the concentration changes of $[ICl_2]^-$ in the solution volume are negligible if small amounts of SO_2 are determined. The pneumatopotentiometric response is therefore peak-shaped. The maximum potential change, corresponding to the peak height, E_p, is a function of the initial amount of SO_2 in the sample. This is the basis of the analytical use of this method. Because the potential is measured under non-equilibrium conditions, the dependence between the AuPME potential changes and the SO_2 content cannot be correlated wih the relations and conclusions valid for the equilibrium potentiometry of redox systems.

EXPERIMENTAL

Apparatus

The experiments were carried out using the pneumatopotentiometric apparatus described in[6], where the preparation of the porous membrane electrode was also described. The metallized membrane used for its preparation was obtained by vacuum vaporization of gold on the porous tetrafluoroethylene membrane Gore-Tex No S 10 363 (W. L. Gore, Elkton, U.S.A.). The reaction vessel of the apparatus, in which the absorbed SO_2 is transferred into the gaseous phase, was filled with 2 ml of 6M-H_2SO_4. Nitrogen was used as the carrier gas; the flow rate of 3.3 ml s^{-1} was used. AuPME was immersed in 50 ml of 10^{-4} to $5 . 10^{-6}$M solution of iodine monochloride in 0·02M-HClO$_4$ containing about $2 . 10^{-4}$M-HCl (see below). The potential of AuPME was measured against the saturated calomel electrode (s.c.e.) (connected with the solution by a bridge with 0·02M-HClO$_4$) using a voltage follower and was recorded by a strip-chart recorder. The whole measuring part of the apparatus was placed into a Faraday cage.

Reagents

Sulfur dioxide was determined in two different absorption solutions. The 0·1M solution of sodium tetrachloromercurate was prepared by dissolving 27·2 g of HgCl$_2$, 11·7 g of NaCl, and 0·1 g of

the Na salt of EDTA in 1 000 ml of redistilled water. 0·01M-NaOH with 7% (v/v) of glycerine was used as the second type of the absorption solution. The SO_2 content in the stock solution of $1 . 10^{-3}$ M-Na_2SO_3 in the absorption agent was determined by iodometric titration. The analyzed samples were prepared by dilution of the stock solution by the respective absorption solution. The sulfite solution was prepared fresh every day. The stock solution of 0·1M iodine monochloride was prepared by mixing the solutions of 11·068 g of KI in 50 ml of water with 7·134 g of KIO_3 in 250 ml of water and with 200 ml of 30% HCl. Water was added up to 1 000 ml to this solution; this solution was 1·9M in HCl. The working solutions were prepared from the stock solution by dilution.

All the reagents were of the analytical grade, redistilled water in quartz apparatus was used. All measurements were carried out at the room temperature (22°C).

Procedure

AuPME and s.c.e. were immersed in the solution of $[ICl_2]^-$ prepared by adding a given volume of the stock solution to 10 ml of 0·2M-$HClO_4$ and water up to 100 ml. After the potential establishment (15—20 min) 6M-H_2SO_4 was pipetted into the reaction vessel and the nitrogen flow was adjusted to $3\cdot3$ ml s^{-1}. After another 20—30 min the potential of the AuPME reached a constant value and then 10—100 µl of the sample solution were injected into the reaction vessel using a microsyringe. After the complete potential change (3—5 min according to the content of SO_2) another sample was injected. The solution of $[ICl_2]^-$ was exchanged daily, the acid in the reaction vessel according to the requirements, *e.g.*, after excess dilution by samples. After the measurements the AuPME was thoroughly washed with water and stored in air.

RESULTS AND DISCUSSION

Choice of Experimental Conditions

The peak height of the pneumatopotentiometric response depends on the concentrations of acid and iodine monochloride in the working solution and on the nitrogen flow rate.

The acid concentration increase influences favourably the oxidation ability and stability of the $[ICl_2]^-$ solution; on the other hand, it hinders the conversion of SO_2 into HSO_3^-. The value of E_p decreases with the acid concentration increase; for the concentration change from 0·02M to 0·2M-$HClO_4$ the decrease of E_p amounts to about 50% for 30 ng of SO_2. The 0·02M concentration of $HClO_4$ is a suitable compromise. This solution has the pH value of about 1·7 so that SO_2 is by about 70% present in the form of HSO_3^- as it follows from the distribution diagram of the SO_2- $-HSO_3^-$ system (for $pK_1 = 1\cdot37$ and $pK_2 = 6\cdot34$). Perchloric acid was used for the adjustment of the $[ICl_2]^-$ solution acidity as the initial equilibrium potential reached fastest its equilibrium value and no gold was dissolved on the AuPME membrane as it is the case in HCl solutions.

The E_p value decreases roughly linearly with the increase of the nitrogen flow rate. Changing the flow rate from 2·3 to 8·0 ml s^{-1} led to the response decrease of about 30% in the case of 30 ng of SO_2. At higher flow rates the pneumatopotentiometric

peaks are narrower and the potential change disappears more rapidly. This is due to the fact that SO_2 from the solution in the reaction vessel is more rapidly transferred into the gaseous phase but — on the other hand — its amount that penetrates through the membrane pores into the oxidizing agent solution decreases[7]. From the point of view of a sufficiently high response and its fast decay the flow rate of 3.3 ml s^{-1} is suitable so that all measurements were carried out with this flow rate.

The calibration curves in Fig. 1 (curves *1, 2, 3*) illustrate the dependence on the concentration of iodine monochloride. From these curves it follows that the more dilute is the $[ICl_2]^-$ solution the higher is the potential change of AuPME for a given amount of SO_2 (the increasing part of the curves) but for lower amounts of SO_2 the independence of the potential on the amount of SO_2 is already reached. It is difficult to explain the shape of the calibration graphs because in course of the determination the AuPME potential can be affected by a series of different redox equilibria ($[ICl_2]^-/I^-$, $[ICl_2]^-/I_2$, eventually I_2/I^-, HSO_4^-/HSO_3^-) and also the diffusion transport process acting against the potential change plays a role. As the process is basically the titration of $[ICl_2]^-$ by HSO_3^- ions it can be assumed that the highest sensitivity of the determination is achieved under the conditions corresponding to the approach to the point of equivalence. Exhaustion of $[ICl_2]^-$ from the immediate vicinity of the electrode results in a conspicuous decrease of sensitivity.

From the analytical point of view it is important that the highest sensitivity of the determination is achieved for low amounts of SO_2. The suitable shape of the calibration graph for the amounts of SO_2 in the sample that are to be determined can be obtained by a proper choice of the iodine monochloride concentration. *E.g.*, for the determinations up to $30-50$ ng of SO_2, the solution with the $[ICl_2]^-$ concentration of $5 \cdot 10^{-6}$ mol l^{-1} is adequate while for the amounts up to $100-150$ ng of SO_2 the $1 \cdot 10^{-4}$ mol l^{-1} solution should be used.

Concentration Dependence

The dependence of E_p on the amount of SO_2 was studied in detail for the $1 \cdot 10^{-5}$M solution of $[ICl_2]^-$ and the results are presented in Fig. 1 (curves *2, 4*). The highest sensitivity of determination, 9 mV ng^{-1}, was found for $5-20$ ng of SO_2. Regression of seven measurements in the linear part of the curve for $0.1-4$ ng of SO_2 yielded the value of 4.27 mV ng^{-1} for the slope with the standard deviation of 0.05 mV. From these results the values of the limit of quantitation of 0.14 ng of SO_2 in 2 ml of the solution (0.07 ppb) and the detection limit of 0.04 ng of SO_2 in 2 ml (0.02 ppb) have been obtained. The relative standard deviation as obtained from ten measurements was 1.4% for 10 ng of SO_2 and 2.5% for 0.5 ng of SO_2. Fig. 2 presents the recorded pneumatopotentiometric response of AuPME for five different amounts of SO_2 in the vicinity of the limit of quantitation. The value of background noise did not exceed 0.1 mV during the measurements.

The results of the determination were the same for both Na_2HgCl_4 and NaOH solutions. However, the time decrease of SO_2 concentration in the NaOH solution is rather high, particularly for low amounts of sulfur dioxide. The pneumatopotentiometric determination was not possible in the absorption solution of formaldehyde that was proposed as a substitute for the toxic and expensive tetrachloromercurate[5]. Sulfur dioxide cannot be released from this solution by the reaction with an acid.

Interfering Substances

The transfer of SO_2 from the solution into the gaseous phase already vouched for a high separation degree from other possible interfering compounds. Therefore only those substances that give by acidification a gaseous product that can be oxidized by iodine monochloride can interfere. A measureable interference was observed only
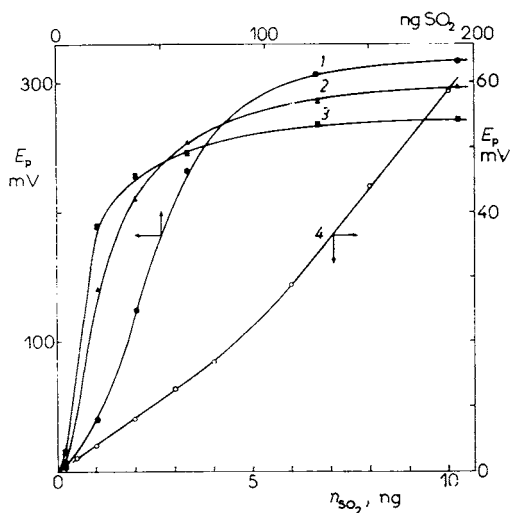

FIG. 1

Dependence of E_p on the amount of sulfur dioxide. Iodine monochloride concentration (mol l^{-1}) in the 0·02M-$HClO_4$: *1* 1 . 10^{-4}, *2* 1 . 10^{-5}, *3* 5 . 10^{-6}. Curve *4*: the concentration dependence in 1 . 10^{-5}M-$[ICl_2]^-$ for low amounts of SO_2. Absorption solution of 0·1M-Na_2HgCl_4, nitrogen flow rate 3·3 ml . s^{-1}
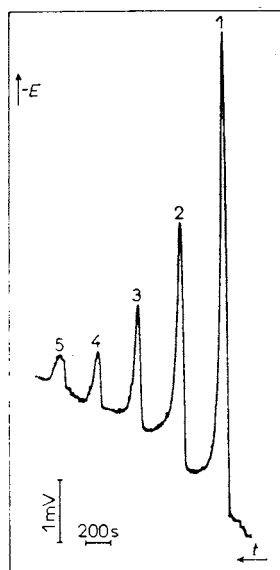
FIG. 2

Pneumatopotentiometric response of AuPME in the solution of 1 . 10^{-5}M-$[ICl_2]^-$. SO_2 amounts (ng): *1* 2, *2* 1, *3* 0·5, *4* 0·2, *5* 0·1. For the experimental conditions — see Fig. 1

in the case of H_2S. For the ratio of amounts $SO_2/H_2S = 1$ in the NaOH solution the resulting ratio $E_p(SO_2)/E_p(H_2S) = 17$. The interference of H_2S is completely eliminated in the determination with Na_2HgCl_4. Nitrogen dioxide, interfering in the photometric determination, does not interfere in the pneumatopotentiometry.

The described method makes possible a highly sensitive determination of sulfites or sulfur dioxide after the absorption in commonly used absorption solutions. The detection limit $(0.02\ ppb)$ is substantially lower than in the case of the pneumato-amperometric determination[8] (100 ppb) or in the case of the use of gas-sensing membrane probes[9] (64 ppb), *i.e.*, in determinations in which SO_2 is also released from the solution into the gas phase. The non-linear concentration dependence (even in the logarithmic scale) is a certain shortcoming of the method. However, the calibration graph has an acceptable shape within three to four orders of magnitude and the highest sensitivity lies in the region of low amounts of SO_2. The pneumatopotentiometric response disappears within about 5 min so that the determination rate is about 10 samples per hour. Low volumes of the analyzed samples with absorbed SO_2 diminish also the consumption of absorption solutions.

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