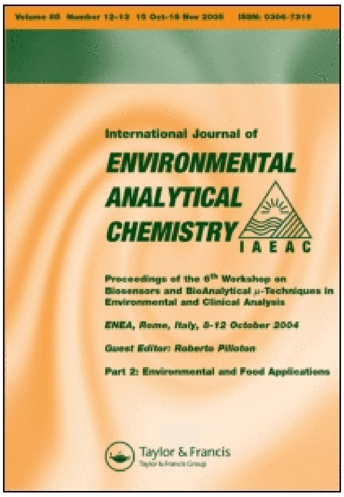

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Spectrophotometric Determination of Atmospheric Sulfur Dioxide with 4(4-Aminophenylazo)-1-naphthylamine

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Spectrophotometric Determination of Atmospheric Sulfur Dioxide with 4(4-Aminophenylazo)-1-naphthylamine

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The use of a *p*-aminophenylazoic dye, *viz.* 4-(4-aminophenylazo)-1-naphthylamine, is proposed as a spectrophotometric reagent for the determination of atmospheric sulfur dioxide absorbed in sodium tetrachloromercurate solutions. Determinations are made in ethanol-dye-formaldehyde systems displaying a red color at a pH value of 1.3. In the presence of sulfur dioxide solutions the red color turns to a blue one, which has a maximum absorption between 600 and 640 nm. The color development is instantaneous and is sufficiently stable to permit absorbance measurements. The reaction is subjected to interferences of nitrogen dioxide but this can be avoided by the use of an appropriate masking agent. The method allows between 0.07 and 2.4 mcg/ml of sulfur dioxide to be determined. The ratio of sulfur dioxide to ligand in the compound was found to be 1:1. The average of the instability constant was calculated to be 2.5×10^{-5}.

INTRODUCTION

Present air pollution aims are not only surveying and controlling of pollution, but also the forecasting of the dispersion of some pollutants in a certain area.

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This task requires as many as possible rapid and continuous chemical analyses to be correlated with the meteorological parameters.

The specific and sensitive spectrophotometric methods for the determination of sulfur dioxide, a generally occurring air pollutant, have several disadvantages, such as multi-step operations, the use of monochromating light devices, or the long time needed for color development.

Previous investigations carried out by the authors were devoted to the study of chromogenic properties of several *p*-aminophenylazo derivatives interacting in formaldehyde-sulfur dioxide systems. In the present paper an attempt was made to find a more sensitive reagent for the determination of sulfur dioxide, and we are now proposing the use of 4(4-aminophenylazo)-1-naphthylamine.

EXPERIMENTAL

Apparatus

A Beckman Model DB recording spectrophotometer was used to record the absorption spectra. A Spekol Carl Zeiss Jena spectrophotometer equipped with 1-cm cells was used for the measurement of absorbances. An Electrofact Model 53A pH meter equipped with a glass electrode was used for the measurement of pH values.

Reagents and Solutions

4(4-Aminophenylazo)-1-naphthylamine is a common dye, *viz*. Disperse Black (C. I. 11635), and is produced by Francolor as "Diazo Noir Acetoquinone N.Z. 50 1350". Of this dye, a solution (0.1%, w/v) in ethanol was prepared. For analytical purposes the dye was purified by recrystallisation from a water-ethanol mixture. Final determinations were performed with a dye portion purified by column chromatography.

The sodium sulfite solution was prepared in distilled water by the dissolution of anhydrous sodium sulfite (Merck reagent grade), and the concentration was determined daily by the iodine-thiosulfate volumetric method. Aliquots of this standard solution were stabilized in 0.04M sodium tetrachloromercurate, so that a final concentration of 10 mcg SO_2/ml was obtained.

A mixture of 5% (w/v) potassium chloride in 1.2M hydrochloric acid was used as a stock buffer solution to ensure that pH values ranged between 1.1 and 1.4.

Aqueous formaldehyde solutions were prepared from a 10% (v/v) stock solution by diluting 40% formaldehyde (Chemapol product). All other reagents were reagent-grade commercial products; wherever possible Merck reagents were used.

STUDY OF COLOR-PRODUCING REACTIONS AND PRODUCTS

Ligand Spectra

The solutions for optical measurements were prepared by diluting 0.4 ml of dye solution, 6 ml ethanol, 2 ml buffer solution, and 0.4 ml formaldehyde solution in 25-ml graduated flasks with distilled water, so that the dye concentration was about 6.05×10^{-5}M. The absorption spectra were recorded in 1-cm glass cells against distilled water as a reference (Figure 1, curve A).

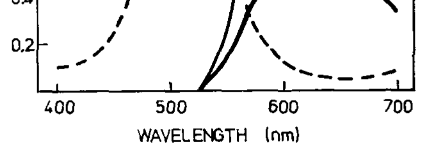

FIGURE 1 Absorption spectra.

A. Ligand spectra recorded against water as a reference.

B. Complex spectra with an excess of SO_2 recorded against water as a reference.

C. Complex spectra with a controlled concentration of SO_2 recorded against a blank as reference.

Complex Spectra

The absorption spectra of the SO_2 complex were recorded using solutions prepared as above but with the addition of sufficient sodium sulfite solution to make sure that no reagent remained unreacted (Figure 1, curve B).

Since the above spectra are not useful for current determinations, complex spectra have been recorded by using solutions prepared by diluting 1.5 ml of dye solution, 5 ml of absolute ethanol, 2 ml of buffer solution, 1.5 ml of formaldehyde solution, and 3 ml of sodium sulfite solution in 25-ml graduated flasks with distilled water. Determinations were performed at room temperature by using blanks prepared in the same way, except for adding the sodium sulfite. The results are shown in Figure 1, curve C. Color development was quite instantaneous, and remained stable for at least 10 min. Examination of ligand and complex spectra shows the optimum wavelength to be on a broad maximum between 600 and 640 nm. For the absorbance determinations a wavelength of 625 nm was selected. This wavelength was used throughout the present work.

The order of addition was always the same: dye, ethanol, buffer solution, formaldehyde solution, and sodium sulfite solution. The ethanol was added to prevent precipitation.

Effects of pH on Final Color

The study of the influence of pH on the formation of the complex compound was made in non-buffered media, with the pH being controlled instrumentally. It was determined that for pH values < 3 the hydrogen ion concentration had no or very little influence on the absorption of the ligand alone.

The formation of the complex was possible even in strong acid media. A study of the influence of pH on the absorption of the compound was made using solutions prepared by diluting 1.5 ml of dye solution, 5 ml of ethanol, different amounts of potassium chloride-hydrochloric acid mixtures, 1.5 ml of formaldehyde solution, and 2 ml of sodium sulfite solution (10 mcg/ml as SO_2) in 25-ml graduated flasks with water. Absorbances were measured with respect to blanks prepared in the same way but without the sodium sulfite solution.

From the shape of the curve in Figure 2 one can see that with pH values ranging between 1.0 and 1.5 the absorption of the compound reaches a plateau, and with a pH value higher than 1.7 measurements are not possible without a photomultiplier device. That is why 2 ml of a solution of 5% potassium chloride in 1.2M hydrochloric acid was used as a buffer (pH 1.3) for determinations made in 25-ml graduated flasks.

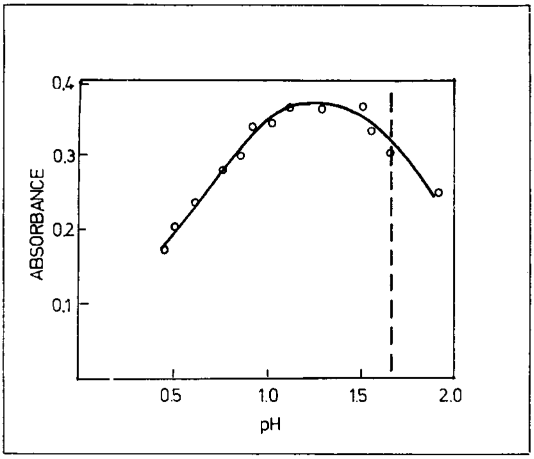

FIGURE 2 Effects of pH on final color.

Effects of Dye Concentration

To determine the optimum conditions for dye concentration a series of solutions was prepared by diluting various amounts of 0.1% dye solution (3.8 mcmole/ml) with 5 ml ethanol, 2 ml of buffer solution, 1.5 ml formaldehyde solution, 2ml sodium sulfite solution and water in 25-ml graduated flasks. Figure 3 shows absorbances measured with respect to blanks plotted versus dye concentrations. With a dye concentration higher than 0.15 mcmole/ml

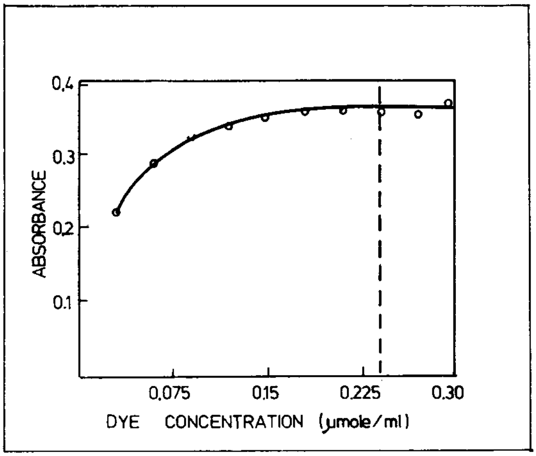

FIGURE 3 Effects of dye concentration.

the maximum sensitivity was reached, and for values higher than 0.24 mcmole/ml no correction was possible for the blank. That is why a concentration of about 0.23 mcmole/ml, i.e. 1.5 ml of 0.1% solution of dye per 25-ml flask, was used in subsequent determinations.

Effects of Formaldehyde Concentration

Optimum concentration of formaldehyde for maximum final color development was studied using test solutions prepared as above but ranging the formaldehyde concentration from 0.1 to 1.0%. As in the West and Gaeke method,[1] it was found that for the given dye-buffer solution the absorbance of test solution increased with formaldehyde concentration until it reached a plateau for 0.53% formaldehyde, i.e. 1 ml of 10% formaldehyde solution per 25-ml flask. For values higher than 0.9% formaldehyde, measurements are not possible without a photomultiplier tube (Figure 4). That is why in the final measurements a concentration of about 0.8% formaldehyde, i.e. 1.5 ml of 10% formaldehyde solution per 25% ml graduated flask, was used.

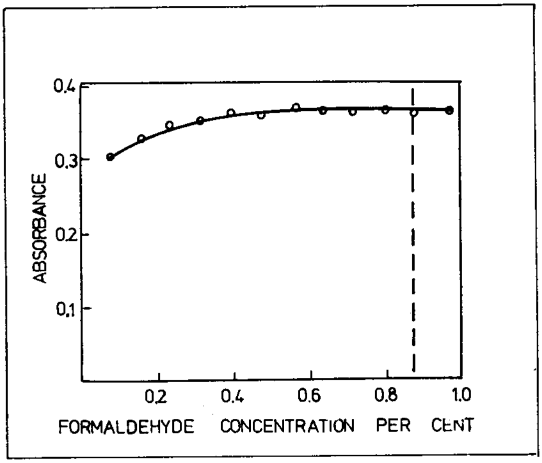

FIGURE 4 Effects of formaldehyde concentration.

Color Development and Time Stability

As mentioned before, the color development was quite instantaneous, the dye displaying a red color, and the compound a deep-blue one, and is sufficiently stable to permit absorbance measurements. The fading of color within a 15-min interval was in the range of systematic errors. The fading of the complex was about 14% for a one-hour delay (see Figure 5, curve A).

When 1 ml of 0.1% *o*-toluidine solution was used to prevent interferences of nitrogen dioxide,[2] the color reached its maximum intensity in 30 min, and was stable for more than 90 min (Figure 5, curve B).

When 1 ml of a solution of 0.6% sulfamic acid was used as a masking agent,[3] the color development was extremely rapid (1–2 min) but the fading was much more rapid than that of the reagent alone (Figure 5, curve C). That is why *o*-toluidine is recommended as a masking agent if nitrogen dioxide is present.

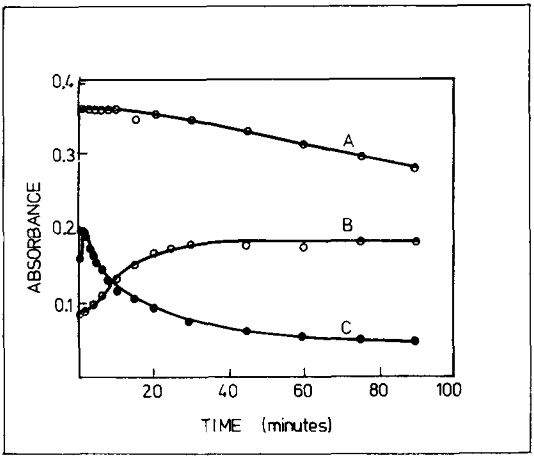

FIGURE 5 Color development and time stability.
A. Without masking agent; B. In the presence of *o*-toluidine; C. In the presence of sulfamic acid.

Stoichiometry and the Instability Constant

By using the mole-ratio method and the method of continuous variation, the ratio of sulfur dioxide to ligand in the compound was found to be 1:1. With the use of the non-isomolar series, the average of the instability constant was found to be equivalent to 2.5×10^{-5}. The necessity for a freshly prepared mixture of ethanol, dye, buffer solution and formaldehyde solution in order for the reagent to be effective leads us to believe that the actual mechanism of the reaction is likely to be different from that proposed by Nauman and West[4] for the determination of the sulfur dioxide with pararosaniline.

RECOMMENDED PROCEDURE

Preparation of Dye-formaldehyde Reagent

Dissolve 0.15 g dye in 650 ml absolute ethanol, add 200 ml buffer solution (5% w/v potassium chloride in 1.2M hydrochloric acid), and dilute up to 1,000 ml with 10% (v/v) formaldehyde solution. If determinations are made using 25-ml graduated flasks, add 10 ml of this dye-formaldehyde reagent to each sample and dilute up to the mark.

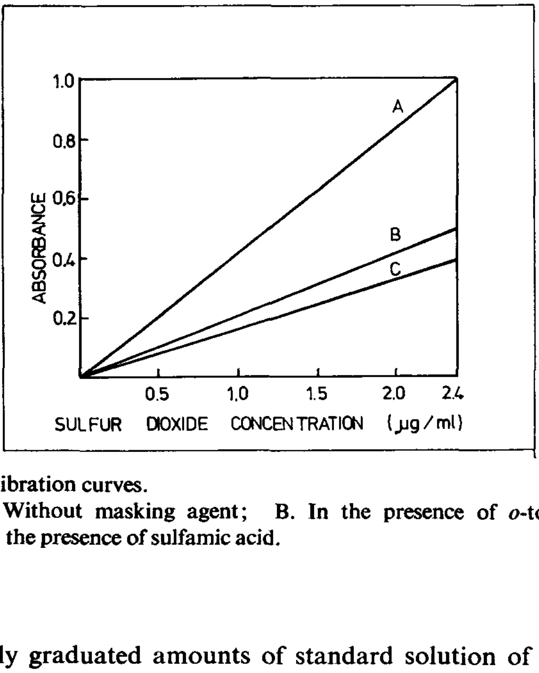

FIGURE 6 Calibration curves.
A. Without masking agent; B. In the presence of *o*-toluidine; C. In the presence of sulfamic acid.

Calibration

Pipet accurately graduated amounts of standard solution of sodium sulfite (10 mcg/ml as SO_2) stabilized in 0.04M sodium tetrachloromercurate. It was determined that, at least within the 0.01 to 0.1M range, sodium tetrachloromercurate had no effect on the color development and its intensity. Add 10 ml of dye-formaldehyde reagent solution and determine the absorption at 625 nm within 10 min, in 1-cm cells, against a blank as reference. In Figure 6, curve A, the absorbances are plotted versus concentration of sulfur dioxide. The method allowed us to determine between 0.07 and 2.4 mcg/ml of sulfur dioxide. The molar absorptivity was about 2.66×10^4.

If 1 ml of 0.1% *o*-toluidine is used as masking agent the absorbance is to be measured after 30 min. The slope of the calibration curve thus obtained is about 2.0 times lower than the slope of the calibration curve without masking agent (Figure 6, curve B). For rapid measurements, a masking agent consisting of 1 ml of 0.6% sulfamic acid can be added to each sample. Absorbance measurements must be made within 1–2 min after the reagent has been added. The sulfamic acid also acts as a suppressor by reducing the slope of the calibration curve about 2.46 times.

CONCLUSIONS

The proposed reagent is suitable for routine measurements of atmospheric sulfur dioxide, and it has the following advantages:

The absorption maxima of the reagent and of the compound are separated by almost 100 nm, and the absorption maximum of the compound is broad enough to allow the use of the simplest colorimeters.

The color development is quite instantaneous.

The deep-blue compound obeys with a good sensitivity the Lambert–Bouguer–Beer law over a wide range of absorbances.

The determination requires the addition of a single multicomponent solution.

It is obvious that the use of such a reagent in a sulfur dioxide spectrophotometric monitor would simplify the apparatus, and avoid the correction factors imposed by the non-instantaneous reaction of the pararosaniline.

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