Spectrophotometric flow injection analysis of formaldehyde in aqueous solutions using 3-methyl-2-benzthiazolinone hydrazone

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Summary. A flow injection method for the determination of formaldehyde was developed. It is based on its reaction with 3-methyl-2-benzthiazolinone hydrazone (MBTH) to yield a blue formazan anion. Typically 180 μl samples are injected into a buffered carrier stream with a frequency of 30 per hour. This sample line merges with the reagent stream containing MBTH, whereupon an azine is formed. After merging with a second stream containing an acidic solution of FeCl₃ as reagent, MBTH is oxidized to an intermediate that attacks the azine yielding the formazan dye with an λ_max at 635 nm. The method was applied to formaldehyde concentrations in the range from 0.15 mg/l to 15 mg/l. The relative standard deviation was 2.3% for 3 mg/l formaldehyde, and 5.1% for 0.3 mg/l, respectively. Strong reducing agents like nitrite interfere seriously. Out of the family of carbonyl compounds only acetaldehyde and propionaldehyde cause strong positive interference.

Introduction

Formaldehyde is widely used in industry for the production and chemical treatment of a variety of products such as resins, fertilizers, explosives, rubber and cotton, and in the synthesis of many organic compounds. Especially in the manufacture of building materials such as particle board, plywood and urea insulation, formaldehyde is a major component. Recently there has been great interest in measuring formaldehyde in indoor environments because outgassing of formaldehyde from these building materials can cause irritation and potential harm to occupants [1, 2].

Monitoring and toxicological studies of formaldehyde exposure, as well as studies on the emission of this chemical from wood products generate large numbers of data to be analyzed. Therefore there is a necessity to replace the time consuming standard procedure, for example described in the guidelines of the Verein Deutscher Ingenieure [3, 4] using pararosaniline and sulphite or 3-methyl-2-benzthiazolinone hydrazone, with a kinetic method, that is very sensitive but requires rigid control of reaction time and temperature for accurate determination. Flow-injection analysis (FIA) can satisfy these requirements and is useful for the analysis of microliter samples.

Although various methods have been developed for the determination of formaldehyde based on spectrophotometry [3 – 7], liquid chromatography [8 – 10], gas chromatography [11 – 13] and enzymatic methods [14], they are either not sensitive enough, require expensive instrumentation, are subject to interferences from other compounds, are not stable enough or have high detection limits. The determination of formaldehyde using FIA with spectrophotometric detection has been reported by several workers [15 – 20]. Based on the pararosaniline method [16, 20], determination of formaldehyde in the range of 1 – 50 μg/ml with a sampling frequency of 40 samples per hour could be achieved. With the photometric determination of formaldehyde by means of the acetylacetone method using a FIA-system 0.1 – 200 mg/l can be determined [15]. Safavi and Ensafi [18] employed the brilliant green-sulphite reaction determining 0.04 – 3 mg/l.

We present a sensitive flow-injection method for trace analysis of formaldehyde based on the specific reaction of C₁ – C₃ aldehydes with 3-methyl-2-benzthiazolinone hydrazone and an oxidizing agent. The proposed method is suitable for the determination of as little as 0.06 mg/l formaldehyde in aqueous solutions. A wide range of formaldehyde concentrations to be determined is covered, depending on FIA parameters like reagent concentration, temperature and length of reaction coils. Also effects of pumping rate, sample volume and interfering compounds on this reaction were studied.

Experimental

Materials and reagents

Analytical grade FeCl₃ and 37% v/v formaldehyde solution were obtained from Merck (Darmstadt, Germany). 3-Methyl-2-benzthiazolinone hydrazone (MBTH) and trishydroxymethane were purchased from Sigma (Deisenhofen, Germany). Bidistilled water was used throughout to prepare reagent and sample solutions. Formaldehyde stock solution (300 mg/l) was prepared by diluting 0.8 ml of 37% formaldehyde solution to 1 l with water and was standardized by using the sodium sulphite method [21]. Formaldehyde solutions were prepared daily from the stock solution by dilution with water. MBTH solution was prepared by dissolving 22 mg MBTH in 100 ml water. As an oxidizing agent 0.2% FeCl₃ was dissolved in 0.4 mol/l HCl. These solutions were prepared daily.
Apparatus

The flow-injection system is shown in Fig. 1. All photometric measurements were performed with a Perkin Elmer UV/VIS spectrophotometer (model 124) equipped with a flow-through cell 178.010 QS from Hellma (Mülheim/Baden, Germany) with an optical pathlength of 10 mm and a cell volume of 70 μl. The data from the photometer were digitalized with an ADDA-card from Humer MC-Technik (Mitterndorf, Austria). The five-channel peristaltic pump from IKA (Staufen, Germany), which can be operated in the range from 2 to 200 revolutions per minute, was fitted with silicon rubber tubes with an inner diameter of 0.5 mm. Mixing coils and tubing consisted of Teflon with an inner diameter of 0.68 mm. The thermostated bath was kept at 60°C. The samples were injected with a Rheodyne 5020 injection valve.

General procedure

The pumping rate for the optimized standard determination of formaldehyde is 1 ml/min for carrier and reagent streams, which are 0.1 mol/l Tris/HCl buffer (C), MBTH solution (R1) and FeCl₃ solution (R2). The 180 μl sample is injected at S into the buffer stream. MBTH solution and the carrier stream are mixed at joint J1. The following mixing coil (C1) is thermostated and joins the FeCl₃ stream at J2. After passing the second mixing coil, the sample traverses through the flow cell into the photometer. For general purposes, the following optimum concentrations and parameters are suggested: MBTH concentration: 1 mmol/l; FeCl₃ concentration: 0.2 g/l; length of mixing coil C1: 200 cm; length of mixing coil C2: 250 cm; λ_max: 635 nm. The reagent and the carrier streams were allowed to flow continuously and the peak heights were measured.

Results and discussion

All preliminary studies were made with a 3 mg/l solution of formaldehyde.

Effects of length of mixing coils

Figure 2 shows only a slight effect of the tube length of the formaldehyde-MBTH mixing coil C1 on the sensitivity. Nevertheless, mixing coils C1 longer than 330 cm decreased the sampling rate without significant increase in peak height. Additionally, the peak heights increase with the increase of the tube length of the colour reaction coil C2 up to a tube length of 200 cm. Due to dispersion, peak broadening and tailing were observed with longer reaction coils, and as a result the peak height decreased with longer reaction coils.

Effects of flow rate and sample volume

The effect of flow rate was investigated (Fig. 3). The peak heights increased as the flow rate decreased. However, because of peak tailing the peak heights decreased extremely with very low flow rates. This could also be observed with sample volumes greater than 200 μl (Fig. 4). In general, the injected sample volume is a powerful tool to change the dispersion of the FIA-system. The steady state signal could be achieved with sample volumes greater than 400 μl. But the extreme peak broadening decreased the sampling frequency to a minimum of 15 samples per hour. Hence 180 μl was chosen as the optimum sample volume for subsequent work.

Effects of reagent concentration

The concentration of the oxidizing agent was kept constant at 0.2 g/l FeCl₃. The effect of MBTH concentration on the