

The special application

Determination of formaldehyde in air by polarography

We would like to thank Prof. Dr. E. Alter, Ms. G. Donnevert (Dipl.-Ing.) and Mr. N. Herler (Dipl.-Ing.) from the Centre for Environmental Technology of the Technical University of Giessen-Friedberg, Germany, for this interesting application.

Introduction

Within the context of his diploma work Mr. Herler has developed a highly sensitive polarographic method for the determination of formaldehyde in air. Formaldehyde is still one of the most important toxic substances found in interior living rooms as it is often used even today; it occurs in chip-board, flooring materials, parquetry floors (parquetry sealing), thermal

insulation panels, plywood, insulating foams, furniture and easy-care textiles. The largest emissions of formaldehyde are caused by industrial plants, furnaces and motor transport.

Formaldehyde has long been recognised and classified as being an extreme health hazard. Even very low concentrations in the air can cause irritation to the eyes and mucous membranes as well as allergies. At higher doses coughs, bronchitis, indisposition and difficulties in breathing and orientation occur. On top of this formaldehyde is regarded as being a possible carcinogen.

Until now photometric analysis methods or HPLC methods have been used for the determination of formaldehyde in air; however, these suffer from several disadvantages. The well-known polarographic determination method (reduction of formaldehyde in alkaline solution at the DME; see Metrohm Application Bulletin No. 196) cannot be used for air analysis because of its inadequate sensitivity.

The newly developed method in which formaldehyde is reduced in acidic solution following the addition of hydrazine has a determination limit of ca. 150 ng (absolute mass in the measuring cell). It is therefore extremely suitable for a wide range of emission and immission measurements. Gas-washing bottles through which the air is drawn are used for sampling.

Instruments and accessories used

- 646 VA Processor
- 647 VA Stand
- Gas-washing bottles (impinger bottles) with frit inserts and a suitable pump for air sampling

Reagents

- Supporting electrolyte:
Hydrazinium sulphate $c(\text{N}_2\text{H}_6\text{SO}_4) = 1.5 \text{ mmol/L}$,
ethylenediaminetetraacetic acid disodium salt $c(\text{Na}_2\text{H}_2\text{EDTA}) = 20 \text{ mmol/L}$,
sodium acetate $c(\text{CH}_3\text{COONa}) = 0.2 \text{ mol/L}$
0.02 g $\text{N}_2\text{H}_6\text{SO}_4$, 0.744 g $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2 \text{ H}_2\text{O}$ and 1.6406 g CH_3COONa are dissolved in distilled water and made up to 100 mL. The supporting electrolyte can be kept for ca. three days.
- Formaldehyde standard solution $c(\text{HCHO}) = 1.000 \text{ g/L}$
This is prepared from a ca. 37% formaldehyde solution whose exact HCHO content is determined iodometrically. The standard solution is freshly prepared each day by dilution.
- Absorption solution:
40 mL distilled water or 15 mL each of distilled water and the supporting electrolyte
Gas-washing bottles (impinger bottles) with frit inserts are used for gas sampling and are filled with the appropriate absorption solution. The volume flow rate is 2 L/min. Figure 1 shows a sampling setup for immission measurements.

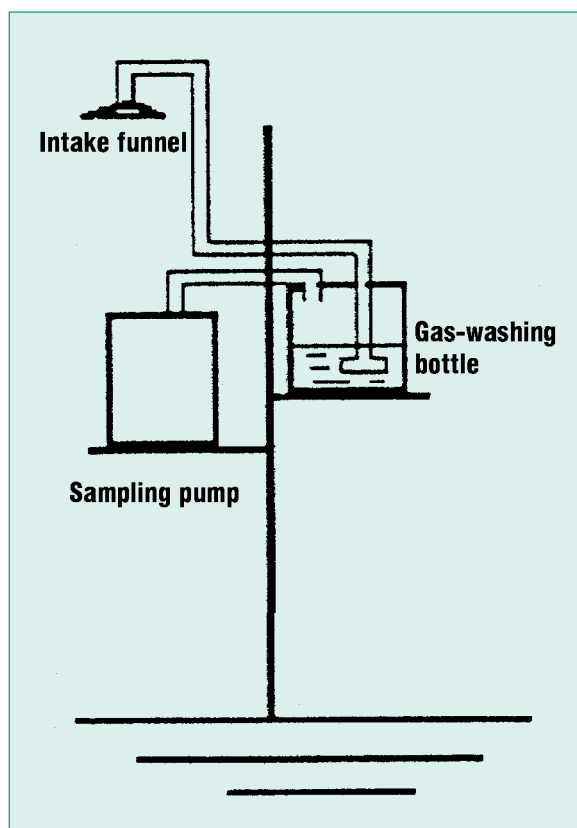


Fig. 1: Sampling setup for atmospheric immission measurements.

Analytical procedure

10 mL sample solution and 10 mL supporting electrolyte (if distilled water is used as the absorption solution) or directly 20 mL absorption solution (if a 1 : 1 mixture of distilled water and supporting electrolyte is used for absorption) are placed in the polarographic vessel and purged for 450 s with nitrogen. A polarogram is then recorded at the DME under the following conditions:

Measuring mode	DP
Pulse amplitude	-50 mV
Initial voltage	-0.7 V
Final voltage	-1.4 V
Sweep rate	8 mV/s

The hydrazone formed from the formaldehyde and the hydrazine of the supporting electrolyte is reduced on the mercury droplets. The peak potential is ca. -1.05 V.

The concentration is determined by standard addition. After each addition, i.e. prior to the measurement itself, the solution is purged for 150 s with nitrogen. Figure 2 shows the polarograms of a formaldehyde determination.

The blank of the supporting electrolyte has to be determined for each analysis and taken into consideration when the result is calculated.

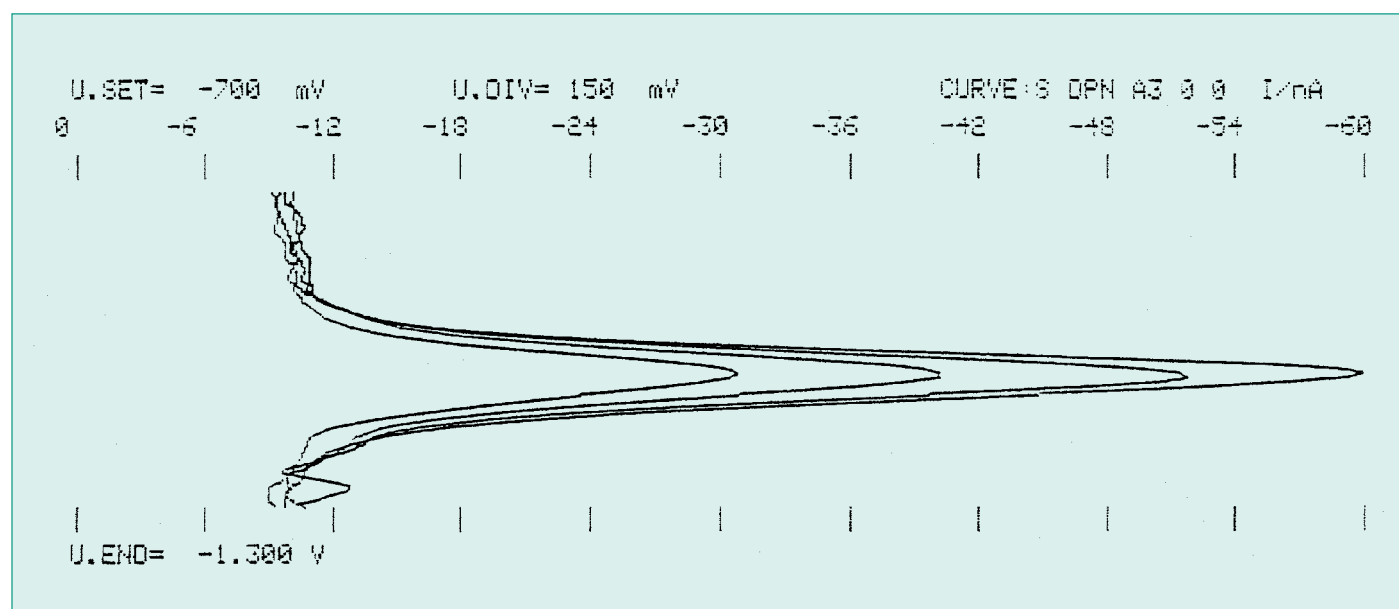


Fig. 2: Polarograms for the determination of formaldehyde.

Results and discussion

The hydrazine method described for the polarographic determination of formaldehyde is exceptionally sensitive. The determination limit is ca. 150 ng (absolute mass in the measuring cell). The linear working range of the method is between 100 ng and 10 μ g formaldehyde. It therefore complements in an ideal way the polarographic determination method in alkaline solution (described in Metrohm Application Bulletin No. 196), which can be used in the range 10 μ g ... 5 mg formaldehyde.

Compared with photometry or HPLC, which were previously used for air analysis, polarography has the great advantage that the standard addition procedure rules out matrix effects. Calibration is carried out in the sample itself, i.e. in the real matrix.

As extensive investigations have shown, the polarographic determination method is extremely suitable for a wide range of different emission and immission measurements. Because of its high sensitivity the method can also be easily used to check stipulated formaldehyde limits such as the interior

guide value of 0.1 ppm (= 0.12 mg/m³) that applies in Germany or the maximum workplace concentration value (MAK value) of 0.5 ppm. Even the mean hourly atmospheric immission values can be determined with the method described above. Under the above-mentioned conditions the determination limit in this case is ca. 1 ppb (= 1.2 μ g/m³).