

Note

Determination of formaldehyde as its lutidine derivative in the atmospheric liquid phase by high-performance liquid chromatography

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Several papers have discussed the important rôle of aldehydes in the atmosphere^{1,2}. Aldehydes are directly injected into the atmosphere by combustion sources and are also produced from the photochemical oxidation of hydrocarbons. As polar molecules, aldehydes are effectively scavenged by hydrometeors. In the atmospheric liquid phase, aldehydes can form adducts with bisulphite (from dissolved atmospheric sulphur dioxide), thus preventing oxidation of S(IV) to S(VI). This reaction is highly important in the production of acidity in the atmospheric liquid phase³.

Formaldehyde is certainly the most abundant carbonyl compound in the atmosphere^{4,5}, but its concentration in the atmospheric liquid phase is always in the micromolar range; therefore highly sensitive and selective analytical techniques are required for its detection. Two methods are described in the literature for determination of formaldehyde at atmospheric concentration levels: (a) as its 2,4-dinitrophenylhydrazone, followed by high-performance liquid chromatographic (HPLC) separation with both UV⁴ and electrochemical⁶ detection; (b) as its lutidine derivative, with spectrophotometric detection^{5,7}.

An HPLC method for the separation of different aldehydes as their lutidine derivatives has also been proposed⁸. In this paper we discuss a similar technique for the determination of atmospheric concentrations of formaldehyde. This method is highly selective and sensitive. Bisulphite interference is also taken into account. The accuracy and reproducibility of the proposed method is assessed using confidence band statistics⁹.

EXPERIMENTAL

Apparatus

A Hewlett-Packard 1010A chromatograph, modified with a Rheodyne 7120 sample injector and a 20- μ l loop, was used. A commercial reversed-phase column containing Erbasil C₁₈, 10 μ m (250 \times 4.6 mm I.D.) was employed for all measurements. Detection was performed with a Metrohm 656 electrochemical detector equipped with a glassy carbon electrode. The surface of the electrode was renewed

every day by mechanical polishing with alumina powder ($0.3 \mu\text{m}$). A silver/silver chloride electrode was used as a reference, together with a Metrohm VA641 potentiostat and d.c. amplifier. A mixture of deionized water (Milli-Q, $18 \text{ M}\Omega$) and methanol (HPLC grade) containing an electrolyte (1 g/l lithium perchlorate and 0.05 g/l sulphuric acid) was used as the mobile phase. An UV-visible spectrophotometer Perkin-Elmer 551 was also used for the analysis.

Analytical procedure

Commercial reagent-grade products were used with no further purification. The lutidine derivatives of the following aldehydes were synthesized: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, *n*-valeraldehyde and isovaleraldehyde. Solutions of $2.65 \cdot 10^{-2} \text{ M}$ formaldehyde and $5.77 \cdot 10^{-2} \text{ M}$ of the other aldehydes were added to 100 ml of an aqueous solution containing 0.2 ml of acetylacetone and 0.3 ml acetic acid (Nash B reagent¹⁰). The reaction products from the C_1 – C_3 aldehydes were purified by recrystallization from ethanol, while the derivatives of butyraldehyde, *n*-valeraldehyde and isovaleraldehyde were separated by concentration, after chromatographic purification on a silica column.

Microscale reactions were performed with formaldehyde in the concentration range of atmospheric interest (0.1 – $100 \mu\text{M}$). Derivatization reactions in the micromolar range were carried out in a sonicator at 60°C and were considered complete after 30 min¹⁰.

RESULTS AND DISCUSSION

Fig. 1 shows a chromatogram of the lutidine derivatives of the six aldehydes examined in this study. The test solutions were prepared by dissolving known amounts of the pure solids in water–methanol (40:60, v/v). Under the described conditions, all compounds are separated except for the *n*-valeraldehyde and isovaleraldehyde derivatives. Table I summarizes the retention data for the lutidine derivatives and the derivatizing agent on an Erbasil C_{18} column.

Fig. 2 indicates the difference in behaviour between formaldehyde and the other aldehydes; it is the only one electrochemically active at a potential lower than +0.6 V.

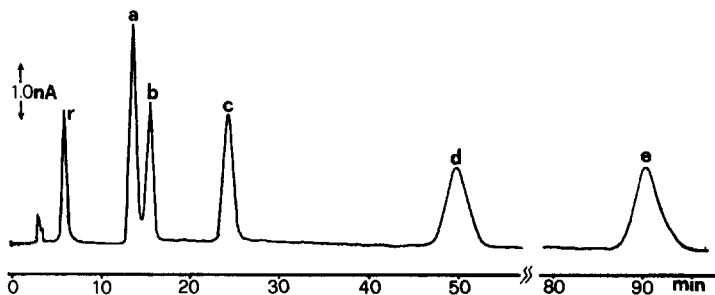


Fig. 1. HPLC separation of aldehydes as their lutidine derivatives: r = reagent; a = formaldehyde; b = acetaldehyde; c = propionaldehyde; d = butyraldehyde; e = *n*-valeraldehyde and isovaleraldehyde. Column: Erbasil C_{18} . Eluent: water–methanol (65.7:34.3, v/v) containing 1 g/l LiClO_4 and 0.05 g/l H_2SO_4 ; flow-rate 1.3 ml/min. Potential: 1.00 V.

TABLE I

HPLC CAPACITY FACTORS, k' , OF THE LUTIDINE DERIVATIVES

Eluent: water-methanol (65.7:34.3, v/v), with 1 g/l lithium perchlorate and 0.05 g/l sulphuric acid; flow-rate 1.4 ml/min. Electrode potential: 1.00 V vs. silver/silver chloride.

Compound	Capacity factor, k'
Derivatizing reagent	0.91
Formaldehyde derivative	2.91
Acetaldehyde derivative	4.00
Propionaldehyde derivative	6.73
Butyraldehyde derivative	15.00
<i>n</i> -Valeraldehyde derivative	27.64
Isovaleraldehyde derivative	27.64

Several experiments were performed at micromolar concentrations of the various aldehydes, representative of the values in the atmospheric liquid phase. These analyses were carried out at a potential of +0.85 V, since under these conditions the peak due to the excess of reagent is minimized.

A recovery study was performed by comparing the peak heights obtained from solutions of the solid derivatives with those obtained from the corresponding micromolar solutions. This showed that the derivatization reaction, at such low concentrations, is quantitative only for formaldehyde, as reported previously by Nash¹⁰.

Sulphite interference

It has been reported^{3-5,7} that aldehyde-bisulphite adducts are formed in sam-

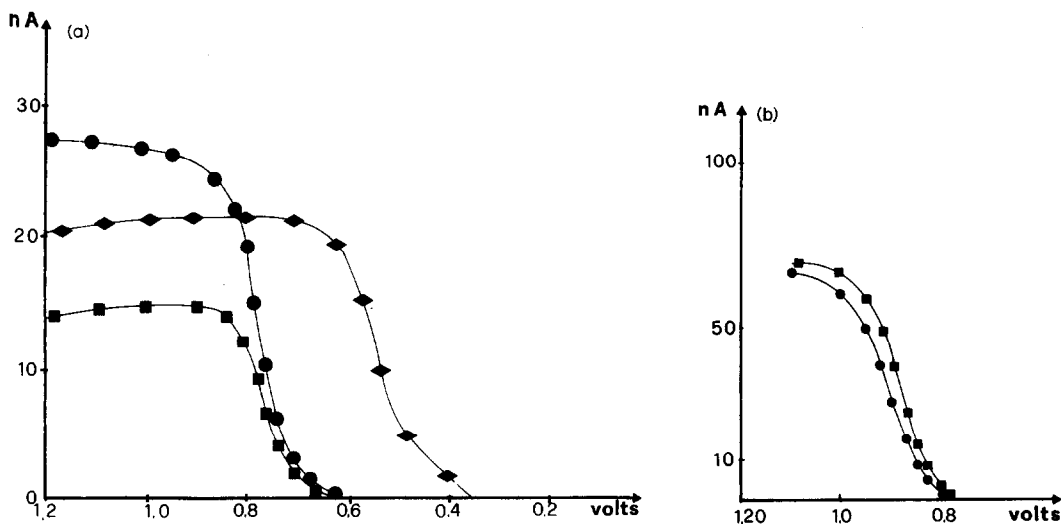


Fig. 2. Relationship between the response of the electrochemical detector and the applied potential for 20 μ M lutidine derivatives. a, \blacklozenge — \blacklozenge , Formaldehyde; \bullet — \bullet , acetaldehyde and propionaldehyde; \blacksquare — \blacksquare , butyraldehyde (chromatographic conditions as in Fig. 1). b, \blacksquare — \blacksquare , Isovaleraldehyde; \bullet — \bullet , *n*-valeraldehyde (same chromatographic conditions as in a except for the eluent: water-methanol (77.7:22.3, v/v) containing 1 g/l LiClO_4 and 0.05 g/l H_2SO_4).

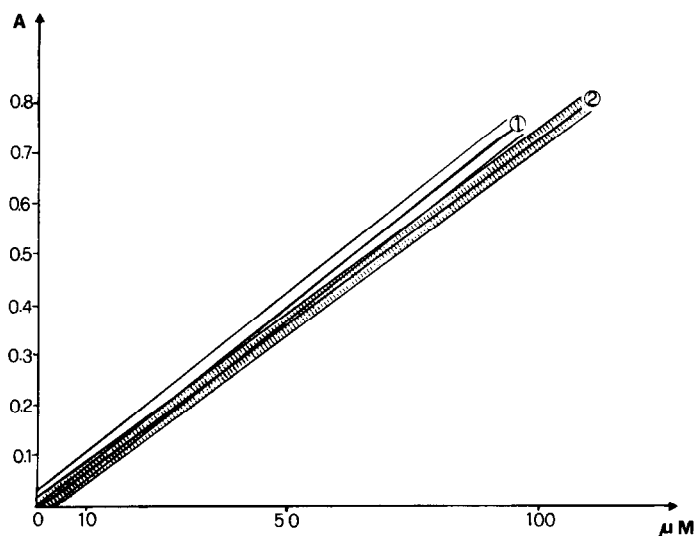


Fig. 3. Calibration plots for spectrophotometric analysis at 412 nm: 1, standards of lutidine derivative of formaldehyde obtained by microscale reaction; 2, as above but with addition of bisulphite and iodine.

ples of the atmospheric liquid phase. This results in an underestimation of the aldehyde concentration. We have taken this possible interference into account in our analytical procedure.

Smith and Erhard¹¹ proposed the addition of iodine in order to oxidize bisulphite in solution. Their results indicate that such addition does not interfere with the formaldehyde determination.

Linear regression plots for standard formaldehyde solutions, analyzed according to the Nash method with spectrophotometric detection at 412 nm, are shown in Fig. 3. Curve 1 represents standard formaldehyde solutions curve 2 the same standards to which bisulphite was added and then immediately oxidized by addition of iodine. The two curves are in reasonable agreement, within the limits of the confidence band (see below).

A further HPLC recovery study of the lutidine derivative of formaldehyde was then performed. Fig. 4 shows the calibration curves obtained for solutions of the pure solid (diacetyldihydrolutidine) in water-methanol (concentration range 0.1–100 μM). A multiplecurve procedure¹² was used, so two different concentration ranges are plotted separately. Fig. 5 presents similar plots for the same range of standards obtained by microscale derivatization reaction, with bisulphite and iodine added. A comparison between Figs. 4 and 5 shows that the slope of the curve obtained from the pure solid is quite different from that obtained by microscale derivatization. Therefore, the calibration curves in Fig. 5 are the most appropriate for analysis of formaldehyde at low concentrations.

Data treatment using confidence band statistics

Since the present procedure is intended for analysis of formaldehyde at very low concentrations, particular care should be taken in determining the accuracy and reproducibility.

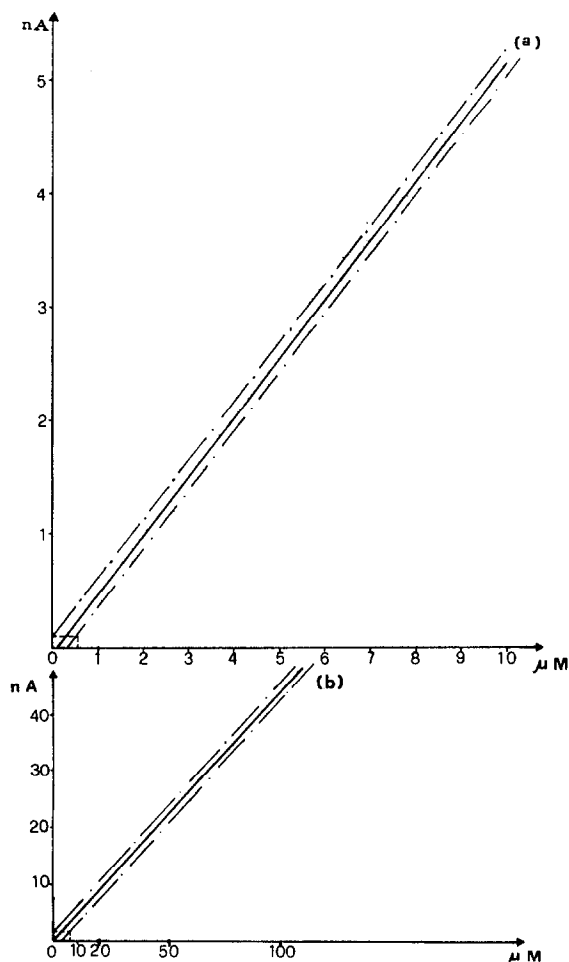


Fig. 4. HPLC calibration plots for the lutidine derivative of formaldehyde obtained by dissolving the pure synthesized solid in methanol-water solution: a, 0–10 μM ; b, 0–100 μM .

The two calibration curves in Figs. 4 and 5 were computed from different combinations of contiguous concentration ranges¹²: (a) 0–10 μM ; (b) 0–100 μM . For each regression plot a confidence band was calculated. This is an estimate of the precision of the sample analysis in terms of all relevant factors¹³. The plot giving the narrowest confidence band around a predicted sample concentration is the most appropriate for that particular sample, and is then used to derive the actual concentration. The statistical procedure indicates that electrochemical detection “works” better in the lower concentration range than spectrophotometric detection.

Particular care was taken in defining the detection limit for our procedure. Usually the detection limit is defined as the lowest concentration at which the analyte can be shown to be present, within a given confidence level⁹. Confidence band statistics provides a useful measure of the minimum reportable concentration, as that at which the confidence band around the predicted sample concentration just includes

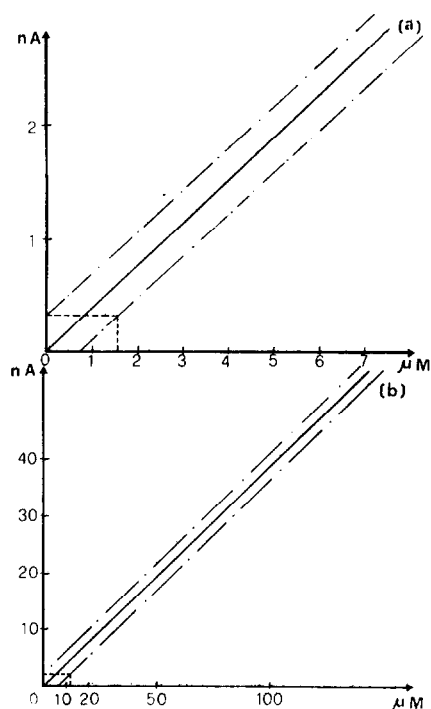


Fig. 5. HPLC calibration plots for the lutidine derivative of formaldehyde obtained by microscale reaction in the presence of bisulphite and iodine: a, 0–10 μM ; b, 0–100 μM .

zero as a lower bound (see Fig. 5). Also, the minimum reportable concentration is usually a factor of 3–10 higher than the detection limits reported in the literature, and is a much more realistic estimate of the level at which the analyte can be shown to be present.

A comparison can be made between different definitions of the detection limit, with reference to our analytical procedure: (i) evaluation from confidence band statistics (see Fig. 5) 1.55 μM ; (ii) evaluation from the standard deviation of a blank, *i.e.*, $4.65 \sigma_{\text{Blank}}^{14,15}$, 0.80 μM ; (iii) evaluation from the signal-to-noise ratio, *i.e.*, 5 S/N, 1.00 μM . The differences between the three methods and the more realistic estimate of the detection limit provided by confidence band statistics are clear.

In the treatment of our data we used an "explicit blank", *i.e.*, the calibration plots were corrected by subtracting the blank signal¹⁶. The complete analytical procedure was used for blanks too.

CONCLUSIONS

The advantages of the present method of formaldehyde analysis with respect to the classical spectrophotometric procedure can be summarized as follows: (a) potential interference of other aldehydes is avoided, since these are separated under the described chromatographic conditions; (b) even in the presence of abnormally high concentrations of other aldehydes it is possible to carry out the analysis at potentials

at which only formaldehyde is detectable; (c) lower detection limits are achieved in HPLC analysis with electrochemical detection, as compared to the Nash modified spectrophotometric method ($1.5 \mu\text{M}$ vs. $5.5 \mu\text{M}$) see Figs. 5 and 3). The use of electrochemical detection offers good prospects for the analysis of formaldehyde, as its lutidine derivative, in the atmospheric concentration range of interest.

A few preliminary analyses of fog water samples collected in the Po Valley (northern Italy) were performed. The results indicate a formaldehyde concentration in the range of $23\text{--}100 \mu\text{M}$, similar to the values reported for other areas⁵. Additional analyses of real samples are now in progress in our laboratory.

ACKNOWLEDGEMENTS

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