Comparison of gas chromatographic and spectrophotometric techniques for the determination of formaldehyde in water ☆

Š. Velikonja*, I. Jarc, L. Zupančič-Kralj, J. Marsel

Department of Chemistry, University of Ljubljana, Aškerčeva 5, Slovenia

Abstract

Formaldehyde was determined in aqueous samples by four different analytical procedures (two spectro-photometric and two gas chromatographic). In the spectrophotometric procedures chromatogropic acid and 3-methyl-2-benzothiazolone hydrazone were used. For gas chromatography either an electron-captive or a flame ionization detector were used, and for sample preparation liquid–liquid extraction in the former and solid-phase extraction in the latter case were used. The concentration range covered was between 0.06 and 20 mg/l. Calibration plots and detection limits were optimized for all four procedures.

1. Introduction

Formaldehyde is a well known pollutant present in both industrial and non-industrial environments. It is a combustion product from many sources, including automobile engines and cigarette smoke [1]. As it is still widely used in the furniture industry [2], as a consequence it can be found in different building materials and furnishings. Formaldehyde is also known to be an irritant of the skin, eyes and nasopharyngial membranes [3] and has also been declared a suspected carcinogen [2] and mutagen [4].

Various methods can be used for formaldehyde determination [1,2]. In this work, two spectrophotometric and two gas chromatograph-ic (GC) methods for the determination of formaldehyde in aqueous solutions were applied. The most frequently used method for the determination of formaldehyde is spectrophotometry with chromotropic acid (1,8-dihydroxy naphthalene-3,6-disulphonic acid) [3,5,6]. Another, less often used, method utilizes MBTH reagent (3-methyl-2-benzothiazolone hydrazone) [7,8]. An important problem associated with spectrophotometric determinations of formaldehyde is the interference of many substances, including acetaldehyde, acroleine, phenol and carbohydrates. For this reason, GC was applied as an alternative method for formaldehyde determination. Because of its high selectivity and efficiency of reaction at room temperature [9], derivatization with 2,4-dinitrophenylhydrazine was chosen. The 2,4-dinitrophenylhydrazine derivatisation products can be determined either by high-performance liquid chromatography (HPLC) [10–14] or by GC with electron-capture

---

detector (ECD) or flame ionization detector (FID) [9,15–18]. However, all analytical methods for formaldehyde determination should permit its determination at concentrations below the maximum allowed concentration in different samples. The maximum allowed concentration of formaldehyde in waste water in Slovenia is 1 mg/l.

The two spectrophotometric methods were compared with the more reliable and rarely used GC–ECD and GC–FID methods. Few data on comparisons of methods for formaldehyde determination could be found in the literature [19].

2. Experimental

2.1. Apparatus

For spectrophotometric determinations a Milton Roy Spectronic 1201 spectrophotometer was used. A Hewlett-Packard Model 5890 A gas chromatograph with electron-capture and flame ionization detectors was used in combination with a Hewlett-Packard HP 3396 Series II integrator.

2.2. Reagents and materials

Formaldehyde solution (ca. 36%), iron(III) chloride hexahydrate and sulphamic acid were purchased from Kemika (Zagreb, Croatia). Chromotropic acid (CTA) (99%), 3-methyl-2-benzothiazolone hydrazone hydrochlorid (MBTH) reagent and gradient-grade toluene, n-hexane and acetonitrile were purchased from Merck (Darmstadt, Germany). Sulphuric acid (95–97%) was purchased from Merck-Alkaloid (Skopje, Macedonia). 2,4-Dinitrophenylhydrazine was purchased from BDH (Poole, UK), and, to avoid high blanks, was recrystallized twice from acetonitrile and stored in a closed glass vial. All solutions were prepared with purified water obtained from a Milli-Q water-purification system (Millipore) if not specified otherwise.

Supelclean 6-ml C_{18} cartridges from Supelco (Bellafonte, PA, USA) were used for the solid-

phase extraction associated with the GC–FID procedure.

2.3. Synthesis of standard

The standard derivative of 2,4-dinitrophenylhydrazine with formaldehyde was synthesized as described elsewhere [20] and recrystallized twice from acetonitrile. The product was stored in polypropylene vials in a dark and cool location prior to use.

2.4. Preparation of standard solutions and reagents

From formaldehyde solution (ca. 36%), a stock solution of formaldehyde at a concentration of ca. 10 g/l was prepared and standardized by the sulphite method [3]. The solution was stored in the dark and used for the preparation of other standards by dilution.

MBTH solution at a concentration of 0.037 g/l was prepared daily in water as reagent A. Reagent B consisted of iron(III) chloride (0.05 g/l) and sulphamic acid (0.09 g/l). A solution of 2,4-dinitrophenylhydrazone was prepared in acetonitrile. All solutions were stored in a dark and cool location.

2,4-Dinitrophenylhydrazine solution (for the GC–FID procedure) at a concentration of 1 mg/ml was prepared weekly by dissolving 10 mg of 2,4-dinitrophenylhydrazine in 1 ml of acetonitrile and diluting with HCl–H_2O (1:3, v/v) to 10 ml and stored in a cool and dark location.

2.5. Analytical procedures

Chromotropic acid procedure

A 5-ml volume of the test solution was transferred into a 50-ml volumetric flask and 1 ml of 5% CTA solution was added. After addition of 43 ml of 50% H_2SO_4, the solution was mixed and closed with a glass stopper. The solution was heated on a water-bath at 100°C for 30 min, cooled and diluted to 50 ml with Milli-Q-purified water. The absorbance was measured against the blank at 572 nm.

MBTH procedure

A 1-ml volume of the test solution was placed into a 10-ml graduated tube and 0.5 ml of reagent A was added and mixed. After 1 min, 1 ml of reagent B was added, and after 10 min the mixture was diluted with water to 10 ml. The absorbance was measured against the blank at 632 nm.

GC–ECD procedure

This was based on a procedure described in the literature [15]; 1 ml of test solution was pipetted into a test-tube with a glass stopper and 1 ml of 2,4-dinitrophenylhydrazine solution was added and mixed. 2,4-Dinitrophenylhydrazone was extracted in 1 ml of toluene. Sodium sulphate was used to dry the toluene phase and the extract was analysed by capillary GC with a ^{63}Ni electron-capture detector and split–splitless injection. A 30 m × 0.32 mm I.D. fused-silica capillary column coated with DB-5 (J&W Scientific, Folson, CA, USA) with a 0.25-μm film thickness was used for chromatographic separation, and the nitrogen carrier gas flow-rate was 1.5 ml/min. The temperatures were as follows: injector, 200°C; detector, 290°C; and column oven, 200°C for 1 min, then increased to 250°C at 2°C/min. The purge activation time was 1 min. Peak heights for 2,4-dinitrophenylhydrazone were used for quantification.

GC–FID procedure

Preconcentration on C_{18} cartridges was based on a procedure described elsewhere [11] with modification, i.e., after sample loading the cartridge was not washed with 17% acetonitrile solution, as 2,4-dinitriophenylhydrazones are eluted with this reagent.

From the stock solution, 0.2 ml of 2,4-dinitrophenylhydrazine solution was added to 100 ml of test solution, shaken and the reaction allowed to proceed for 1 h. The cartridge was activated with 20 ml of acetonitrile and 10 ml of water. The sample was pumped through at a flow-rate of ca. 5 ml/min. After passing all the sample, the cartridge was dried with air and 2,4-dinitrophenylhydrazones were eluted with 3 ml of acetonitrile. The solvent was evaporated with

nitrogen, the residue was dissolved in 1 ml acetonitrile and the solution was analysed by capillary GC with a flame ionization detector and split–splitless injection. A 25 m × 0.20 mm I.D. fused-silica capillary column coated with HP-1 (Hewlett-Packard, Geneva, Switzerland) with a 0.22-μm film thickness was used for the separation, and the helium carrier gas flow-rate was 0.8 ml/min. The make-up gas was nitrogen. The temperatures were as follows: injector, 200°C; detector, 280°C; and column oven, 150°C for 1 min, then increased to 250°C at 3°C/min. The purge activation time was 1 min. Peak areas for 2,4-dinitrophenylhydrazone were used for quantification.

3. Results

3.1. Calibration

Calibration was performed with standard aqueous solutions of formaldehyde in tap water for all procedures and the linear regression analysis data are given in Table 1. With the CTA and GC–ECD procedures, each calibration point corresponds to a single analysis, while triplicate analyses were used with the MBTH and GC–FID procedures. Using the procedures described, formaldehyde can be determined in aqueous solutions over a wide concentration range. Each procedure covers a different concentration range, the CTA procedure from 1 to 20 mg/l and the MBTH procedure from 0.06 to 4 mg/l.

The major problem encountered with spectrophotometric methods for formaldehyde determination are interferences, hence these methods

Table 1
Regression parameters associated with calibration data

Procedure	a	b	r	$S_{y/x}$
CTA	0.0016	0.0487	0.9997	0.0069
MBTH	0.0004	0.1912	0.9998	0.0040
GC–ECD	0.5160	0.4334	0.9973	0.3977
GC–FID	0.3890	0.3775	0.9972	0.2762

are not reliable. GC methods do not suffer from interferences, but they are less precise (i.e., manual injection, etc). The GC–ECD procedure is capable of determining formaldehyde at concentrations between 0.8 and 10 mg/l, but saturation of the electron-capture detector at higher concentrations limits its linear range. The GC–FID method does not suffer from this problem and is capable of determining formaldehyde in the concentration range between 0.06 and 1 mg/l.

3.2. Recovery studies

To find the recovery of the extraction, 100 ml of a solution of 2,4-dinitrophenylhydrazone were prepared and treated as though it was a test sample. After preconcentration, 2 μl were injected into the gas chromatograph and the peak areas for 2,4-dinitrophenyl-hydrazone were compared with the areas obtained for pure standard solutions. Each experiment was repeated tree times. The recoveries were found to be between 87 and 101% for concentrations of formaldehyde between 3.0 and 0.1 mg/l.

3.3. Detection limit estimates

As formaldehyde is also of great concern in atmospheric chemistry research, e.g., tropospheric ozone formation, the detection limit for analytical methods is of interest. As is well known, Kaiser's approach to the estimation of the detection limit is most widely used [21], but it does not take into account β errors, that is, the possibility of false-positive results, and errors associated with the calibration graph. Long and Winefordner [22] proposed a different approach for the estimation of detection limits, which includes errors in the calibration graph, but still fails to consider β errors. A computer program, Detarchi [23], is based on the hypothesis testing method [24]. This makes it possible to choose the magnitude of α and β errors (the probability of false-positive and false-negative results) and thus these errors can be adjusted depending on the problem. In our work we chose α to be equal to β (0.05).

Table 2
Detection limit estimates

Procedure	Detection limit (mg/l)		
	Kaiser's method	Error propagation method[a]	Detarchi program[a]
CTA	0.15	0.27	**0.41**
MBTH	–	**0.06**	0.04
GC–ECD	0.05	**0.72**	0.60
GC–FID	–	0.04	**0.06**

[a] Finally accepted detection limit estimates are printed in bold.

Blank determinations were repeated for all procedures and the detection limits estimated are given in Table 2. From the data in Table 2, the following conclusions about the estimation of the detection limit can be made. With the CTA and GC–ECD procedures, the detection limit estimates vary widely. The reason is that there are only a few calibration points near the detection limit and only one analysis was made for each calibration point. Detection limit estimates for the MBTH and GC–FID procedures are much closer, because there are more points in the lower concentration range and because every point corresponds to triplicate analysis. This makes the detection limit estimate lower, because there is lower uncertainty about the behaviour of the analyte near the detection limit region. Careful calibration design is essential for good detection limit estimates, as well as repetition of blanks. Careful attention must be paid to calibration points near the detection limit, and the calibration must be repeated several times to obtain sufficient information about the behaviour of the analyte over the whole calibration range and near the detection limit.

3.4. Water analysis

For the analysis of waste water with the CTA and GC–ECD methods, the sample was obtained from a retention pool in a factory that produces phenol–formaldehyde resins. A sample was taken in a glass bottle, which was closed immediately after sampling and was analysed on

the same day. For the CTA and GC–ECD procedures, the standard addition method was employed, because it was assumed that the sample contains phenol, which interferes with the analysis. The standard addition method was employed with three additions. The formaldehyde concentration in this waste water was found to be 0.9 mg/l with both methods, which is below the maximum allowed concentration for waste waters (1 mg/l).

River water was taken from a very polluted river in the region of Ljubljana (Slovenia) and analysed by the MBTH and GC–FID methods. A sample was taken in a glass bottle that had been prerinsed with river water. Each sample was taken at the surface in the countercurrent, closed with a glass stopper, transported to the

laboratory and analysed on the same day. The standard addition method with six points was used for the MBTH procedure, but the estimated concentration of formaldehyde was found to be below the detection limit estimated for the MBTH procedure.

For the GC–FID procedure, three analyses were made and a typical chromatogram is shown in Fig. 1a. The peak height is negligible, because it lies on the tail of another peak. To confirm this small peak, the sample was spiked with 0.05 mg/l of formaldehyde and three additional determinations were made. The peak for 2,4-dinitrophenylhydrazone increased (Fig. 1b). The estimated concentration of formaldehyde in this water sample was below the limit of detection, which means that the concentrations of form-
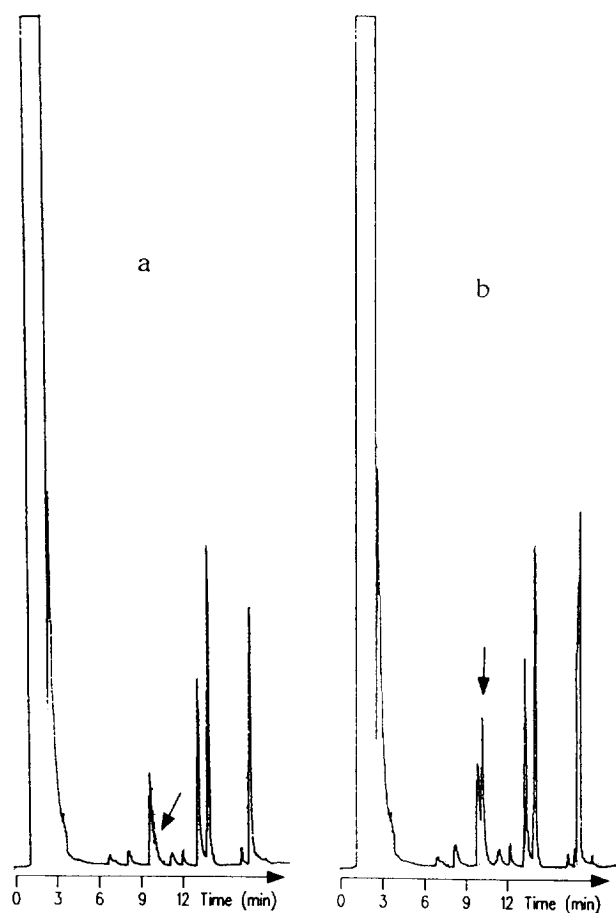

Fig. 1. Chromatograms of (a) river water and (b) river water spiked with 0.05 mg/l of formaldehyde.

aldehyde in that water were at approximately the same level as found elsewhere [4,11,14].

4. Conclusions

Both spectrophotometric procedures described suffer from interferences and therefore cannot be used for formaldehyde determination in water samples including interfering substances.

The GC–ECD procedure includes liquid–liquid extraction of 2,4-dinitrophenylhydrazone into toluene and its injection into the gas chromatograph. At higher concentrations the detector becomes saturated and this narrows the linear range. The GC–FID procedure uses a solid-phase extraction of 2,4-dinitrophenylhydrazone on C_{18} cartridges and is able to cover a lower concentration range than the GC–ECD procedure.

The use of spectrophotometry allows formaldehyde determination in aqueous samples in the concentration range between 0.06 and 20 mg/l, and GC in the range between 0.06 and 10 mg/l.

If proper instrumentation is available, these methods can be used for the determination of formaldehyde in aqueous solutions over a broad concentration range. GC procedures are also a good alternative to the HPLC determination of formaldehyde, which is widely used [10–14].

Detection limit estimates for all four procedures show how important the calibration design is for detection limit estimation. If few calibration points are used for concentrations near the detection limit and with no replicates, the estimated detection limit can be very low, which can lead to false-positive results.

Acknowledgements

References

[1] A.D. Pickard, and E.R. Clark, Talanta, 31 (1984) 763.
[2] M.P. Munoz, F.J.M. de Villena Ruenda and L.M.P. Diez, Analyst, 114 (1989) 1469.
[3] J.F. Walker, Formaldehyde, Robert Krieger, Huntington, NY, 3rd ed., 1975.
[4] F. van Hoof, A. Wittock, E. van Buggenhout and J. Janssens, Anal. Chim. Acta, 169 (1985) 419.
[5] A.P. Altshuller, D.A. Miller and S.F. Sleva, Anal. Chem., 33 (1961) 621.
[6] E. Sawicki, T.R. Hauser and S. McPherson, Anal. Chem., 34 (1962) 1460.
[7] T.G. Matthews and T.C. Howell, J. Air Pollut. Control Assoc., 31 (1981) 1181.
[8] E. Sawicki, T.R. Hauser, T.W. Stanley and W. Elbert, Anal. Chem., 33 (1961) 93.
[9] V.P. Uralets, J.A. Rijks and P.A. Leclercq, J. Chromatogr., 194 (1980) 135.
[10] P.J. Whittle and P.J. Rennie, Analyst, 113 (1988) 665.
[11] R.J. Kieber and K. Mopper, Environ. Sci. Technol., 24 (1990) 147.
[12] K. Fung and D. Grosjean, Anal. Chem., 53 (1981) 168.
[13] A. Benassu, A. Semenzato and F. Zaccaria, J. Chromatogr., 502 (1990) 193.
[14] K. Takami, K. Kuwata, A. Sugimae and M. Nakamoto, Anal. Chem., 57 (1985) 243.
[15] A.L. Pertsovskii and L.M. Kremko, Zh. Anal. Khim., 40 (1986) 1115.
[16] L.J. Papa and L.P. Turner, J. Chromatograph. Sci., 10 (1972) 744.
[17] T. Dumas, J. Chromatogr., 247 (1982) 289.
[18] K. Buckley and L. Fisher, J. Assoc. Off. Anal. Chem., 69 (1986) 655.
[19] M. Petreas, S. Twiss, D. Pon and M. Imada, Am. Ind. Hyg. Assoc., 47 (1986) 276.
[20] Vogel's Textbook of Practical Organic Chemistry, Longman, Harlow, 4th ed., 1978.
[21] P.C. Meier and R.E. Zünd, Statistical Methods in Analytical Chemistry, Wiley, New York, 1993.
[22] G.L. Long and J.D. Winefordner, Anal. Chem., 55 (1983) 712A.
[23] L. Sarabia and M.C. Oritz, Trends Anal. Chem., 13 (1994) 1.
[24] C.A. Clayton, J.W. Hines and P.D. Elkins, Anal. Chem., 59 (1987) 2508.