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Short communication

New derivatization method for determination of 3-chloro-4(dichloromethyl)-5-hydroxy-2(5H)-furanone in water

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Abstract

An extremely potent mutagen, 3-chloro-4(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) is commonly present in chlorinated drinking water. Due to its high mutagenic activity and according to World Health Organization guidelines its concentration should be controlled in drinking waters. Determination of MX is difficult due to ppt levels at which the compound usually exists in drinking waters. Derivatization of MX with 2-propanol is presented as a method which significantly lowers the GC–MS detection level compared to other alcohol derivatization agents. © 1997 Elsevier Science B.V.

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1. Introduction

Surface water is the main source of drinking water in many countries. Chlorination of the water is, for technological and economical reasons, the commonly used method of disinfection despite the fact that some of the numerous chlorination by-products are considered potentially harmful to human health. Chlorination by-products such as chloroform and other trichloromethanes have been known for over 20 years [1,2]. In 1986, a strongly mutagenic compound, i.e. 3-chloro-4(dichloromethyl)-5-hydroxy-2(5H) furanone (MX), was identified in chlorinated waters [3]. Its presence in tap waters was confirmed in many countries [4], also in Poland [5]. Commonly, about 30% of the mutagenic activity of drinking water is due to MX [6–8]. The mutagenic activity of MX is comparable with the activity of aflatoxin [9]. Due to its high activity and common presence in tap water, the World Health Organization has placed MX on the list of disinfection by-products potentially hazardous to humans. Yet, due to the lack of adequate toxicological data and rather complicated analytical procedure no guidelines for MX in drinking water have been established [10].

The commonly applied procedure for MX determination [11] consists of methylation of the compound in 2% sulfuric acid in methanol and GC–MS analysis. The procedure obtains both qualitative and quantitative results providing that SIM (selected ion monitoring) mode in the GC–MS system is used. The ions selected are the triplet

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cluster at m/z 199, 201 and 203. For a further description of the procedure see Ref. [11]. Qualitative analysis is based on identical retention time and peak intensity ratios of the cluster in the sample and the standard of MX.

The current work is concerned with the search for a new derivatization method for MX. The objective was to find a derivatization agent that produces intense fragment ions useful for SIM determination of MX in drinking water extracts.

2. Experimental

2.1. Standards and reagents

MX was synthesized by a method slightly modified from that of Padmapriya et al. [12] and Franzeń and Kronberg [13]. The following reagents were used: methanol and 2-propanol (Fluka), puriss. for residual analysis (GC), ethanol (Fluka), puriss. absolute (GC), pentafluoro-1-propanol (Fluka), purum (GC) and sulfuric acid (Fluka), analytical-reagent grade 95–97%.

2.2. Derivatisation procedures

The MX was derivatized with the following alcohols: methanol, ethanol, 2-propanol and 2,2,3,3,3-pentafluoro-1-propanol. Pentafluoropropanol was used by Ogawa et al. [14] for MX determination with GC–electron-capture detection (ECD). The sample derivatized with methanol was used as a reference.

Four separate samples (standards) containing the same amount of MX (7.5 μg per sample) were separately derivatized with 2% alcoholic H_2SO_4 solution, under the following conditions: methanol and ethanol at 70°C for 1 h; pentafluoropropanol at 70°C for 0.5 h (according to Ref. [14]); 2-propanol at 85°C for 1 h.

All derivatized samples were extracted with three portions of 0.25 ml *n*-hexane. The extracts were combined in 1:1:1:1 volume ratio and analyzed by GC–MS. The 199, 201, 203 m/z fragment abundances were compared.

2.3. Apparatus

A Hewlett-Packard 5890 gas chromatograph coupled with a low- resolution Hewlett-Packard 5971A mass-selective detection (MSD) system was used. A GC HP-1 fused-silica capillary column (25 m×0.25 mm I.D., 0.25 μm) was used.

GC parameters: injection mode, split–splitless; injector temperature, 220°C; injection volume, 2 μl. Carrier gas: helium, pressure 37.7 kPa, flow 0.7 ml/min, linear velocity 30.8 cm/s. Temperature program: 80°C (2 min) at 8°C/min to 220°C at 20°C/min to 280°C (5 min).

MS parameters: resulting voltage, 1400.0 V; interface temperature, 280°C; EI, 70 eV; mass range, 40–400; solvent delay, 5.00 min; data processing system, MS Chem Station.

3. Results and discussion

Prior to GC–MS determination of MX in drinking water extracts, the compound is derivatized with acid methanol in order to convert the hydroxy group to a methoxy group. The most abundant fragment ions in the mass spectrum of the pseudomethylester are the ions at m/z 147 and 149 (Fig. 1) formed by cleavage of the dichloromethyl group from the molecular ion. Despite the intensity of these ions, they are not specific enough for determination of MX in the very complex drinking water extracts. Therefore, the fragment ions at 199, 201 and 203 have been used in the GC–MS-SIM analysis. The disadvantage of this method is the low relative abundances of the cluster ions which are 12.6% (199), 21.5% (201) and 13.2% (203). The ions are formed by loss of the methoxy group from the molecular ion. Due to simultaneous loss of carbon monoxide from the $[M-1]^+$ ion (producing m/z 201) the ratio of the ion cluster at 199 is not the theoretical one (100/97/32 [15,16]) for a fragment that contains three chlorine atoms, but the ratio is 58/100/61. Only by use of a high-resolution mass spectrometer it is possible to distinguish between fragment ions produced by the loss of OCH_3 and of (H+CO) [16]. The main disadvantage with the use of fragment ions at 199, 201 and 203, is that they are of rather low abundance and

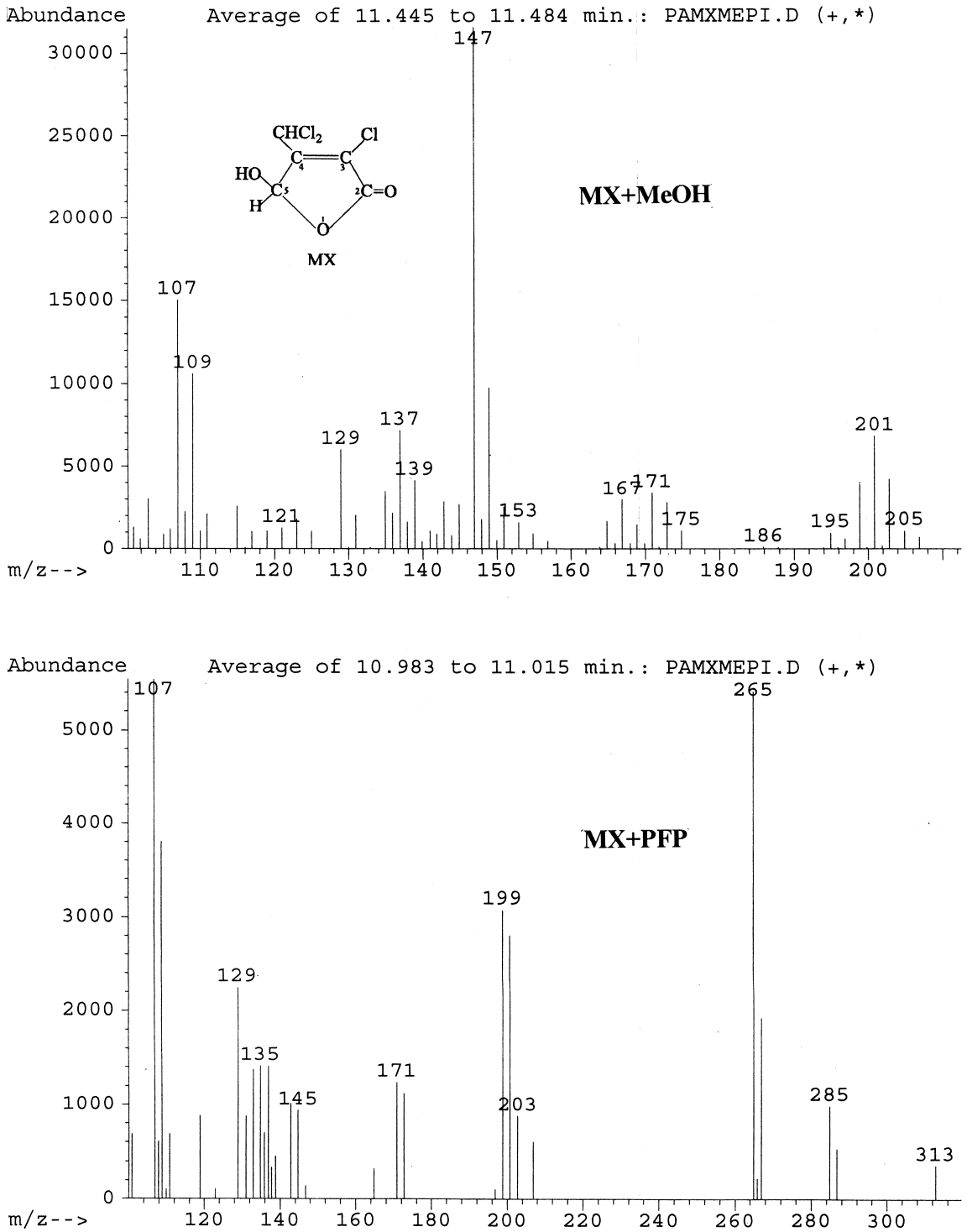

Fig. 1. Full scan spectra of MX derivatized with methanol (MX+MeOH) and pentafluoropropanol (MX+PFP).

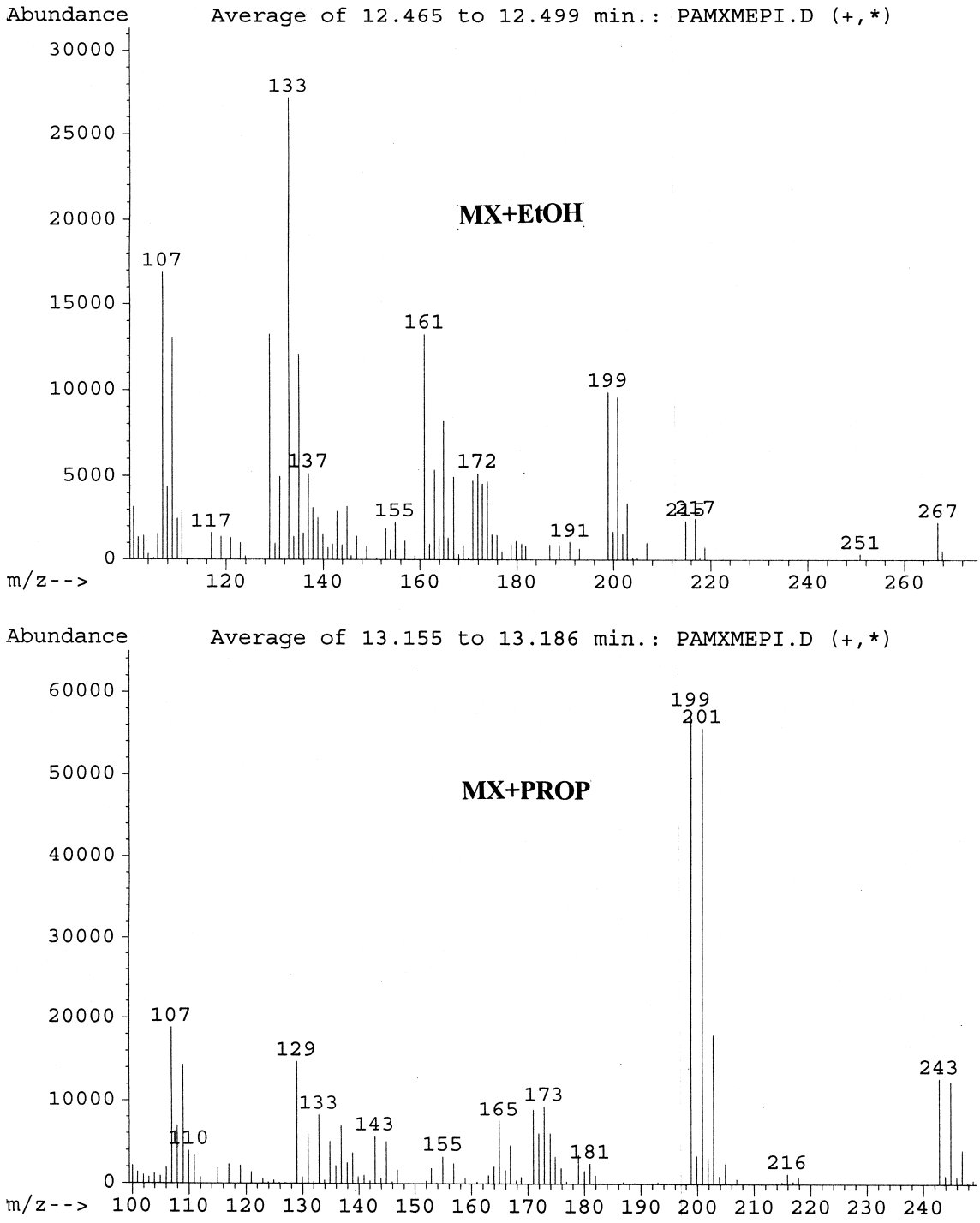

Fig. 2. Full scan spectra of MX derivatized with ethanol (MX+EtOH) and 2-propanol (MX+PROP).

thus render it difficult to detect of low amounts of MX (Fig. 1).

We have derivatized standards solution of MX, with the following alcohols: methanol, ethanol, 2-propanol and 2,2,3,3,3-pentafluoro-1-propanol. The extract of derivatives was mixed in 1:1:1:1 volume ratio. As the peaks of the derivatives are easily separable, such a procedure allowed us to compare directly a sum of two factors: (i) the yield of the derivatization reaction and (ii) the intensities of the cluster ions.

Since the surface areas of the peaks are comparable, the yields of the derivatization reaction are similar. Thus the differences in clusters ion intensities result from different fragmentation peaks of the four derivatives.

In Table 1 the intensities of the cluster ions are compared.

In the mass spectra of the ethyl-, 2-propyl- and pentaflouropropyl the M-OR fragments were observed and the ratio between the ions in the cluster was near the theoretical one for a fragment containing three chlorine atoms, i.e., 100/97/32 (Figs. 1 and 2, Table 1) [15].

The most intense M-OR fragment ions were produced by the pseudo-2-propylester, and these ions were almost ten-times more intense than those formed by loss of M-OCH_3 from the methylated derivative. The M-OR ions produced from the pseudoethylester were slightly higher in abundance and those formed from the pentafluoropropylester were somewhat lower in abundance than the corresponding ions formed from methylated MX.

4. Conclusions

Derivatization with 2-propanol distinctly lowers the detection level of MX in the GC–MS system; particularly in a case when a low-resolution spectrometer is used.

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Table 1
M-(alkoxyl group) fragment peak abundances and relative abundance ratios for MX derivatized with various alcohols

No.	Alcohol used	Retention time (min)	*m/z* fragments	Normalized intensity[a]	Relative abundances of fragment ions *m/z* 199, 201, 203 (%)
1	Methanol[b]	11.46	199	7	56±1.8
			201	12	100
			203	7	63±1.4
2	Ethanol[c]	12.48	199	17	100
			201	16	97±0.5
			203	6	34±0.7
3	Pentafluoropropanol[d]	11.00	199	5	100
			201	5	91±1.7
			203	1.5	30±1.5
4	2-Propanol[e]	13.17	199	100	100
			201	96	96±1.4
			203	31	31±1.4
5	Theoretical [15]		199		100
			201		97
			203		32

[a] The results are normalized to the intensity of *m/z* 199 ion resulting from the fragmentation of pseudo-2-propylester of MX.
[b] $n=5$; [c] $n=4$; [d] $n=3$; [e] $n=5$.

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