Pyrolysis–gas chromatography of chloroorganic compounds in precipitation

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Abstract

A study was undertaken to investigate whether pyrolysis–gas chromatography (Py–GC) can be used to analyse organic compounds, in particular chloroorganic compounds, present in precipitation. Samples of rain and organic extracts of such samples were evaporated to dryness, and the solid material thus obtained was then analysed by combining Py–GC with atomic emission detection or mass spectrometry. The chemical structure of the detected pyrolysis products showed that carbohydrates and nitrogen-containing biopolymers were abundant in the analysed precipitation samples. In addition, several chloroorganic compounds, e.g. chloromethane, chloroacetamides, chloroacetonitriles, chloronitromethanes, chloropyridine, chlorobenzene and phosgene oxime, were identified as pyrolysis products. However, the detected chlorinated structures were not necessarily present in the original samples. Experiments in which chloride enriched with respect to ^{35}Cl was added to the samples showed that new chlorine–carbon bonds were formed during pyrolysis. For example, chloromethane was formed when methanol reacted with HCl. The chlorinated flame retardant tris(2-chloroethyl)phosphate was detected in the pyrolysate, which illustrates that some organic compounds were transferred to the GC system without being thermally degraded. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Pyrolysis; Water analysis; Organochlorine compounds

1. Introduction

Systematic studies of organic compounds in rain and snow have shown that only a minor fraction of the chlorinated organic matter in such media is amenable to conventional gas chromatographic analysis [1,2]. Although the total amount of organically bound chlorine that can be detected as AOX (adsorbable organic halogens) or AOCl (adsorbable organic chlorine) normally ranges from 1 to 30 μg l^{-1} (e.g.

[3]), gas chromatographic analysis with atomic emission detection (GC–AED) has revealed only a few chloroorganic compounds in concentrations exceeding 1 ng l^{-1}, measured as chlorine. The major part of the AOX consists of organohalogens of low volatility and unknown structure [2]. This raises the question of whether or not pyrolysis can render a larger fraction of the chloroorganic compounds present in precipitation amenable to GC.

Thus far, pyrolysis–gas chromatography (Py–GC) has been used primarily to analyse samples of industrially produced polymers, wood and wood products [4,5]. However, Py–GC has also been

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applied to characterise concentrates of organic matter from soil and natural waters [6–8] and to screen for anthropogenic compounds in polluted soils and sediments [9]. The present study represents the first attempt to use Py–GC to characterise organic matter found in precipitation. Our main objectives were as follows:

(i) to investigate the impact of pyrolysis conditions on the yield of pyrolysis products

(ii) to identify the major classes of chlorinated and non-chlorinated compounds produced by pyrolysis of organic compounds enriched from precipitation

(iii) to determine whether the presence of inorganic chloride in the original sample can cause formation of chloroorganic pyrolysis products.

2. Experimental

2.1. Pyrolysis conditions

Two types of pyrolysis devices were used, a coil pyrolyser and a platinum filament pyrolyser. With the former, the sample was placed in a quartz tube surrounded by a coil that was heated for 10 s to induce pyrolysis at 400°C. The equipment used, 120 Pyroprobe, was manufactured by Chemical Data System, PA, USA.

When using a platinum filament pyrolyser, the sample was placed on a metal ribbon (filament). Volatile organic compounds were removed by purging the pyrolysis chamber with nitrogen (15–20 ml/min) at 150°C. The platinum filament was then resistively heated to a pre-set temperature for 8 ms, and the sample was pyrolysed for 2 s. Two pyrolysis options were tested: (i) isothermal pyrolysis at 400°C; (ii) stepwise (fractionated) pyrolysis carried out sequentially at 400, 600 and 750°C. The equipment used was a Pyrola filament pyrolyser manufactured by Pyrol, Lund, Sweden.

2.2. Pyrolysis–gas chromatography

The pyrolysis units were coupled to gas chromatographs equipped with atomic emission detection (Py–GC–AED) or mass spectrometric detection

(Py–GC–MS). In both cases, pyrolysis products were transferred on-line to the gas chromatographs.

2.2.1. Py–GC–AED

Py–GC–AED analyses were carried out on a Hewlett-Packard 5890 gas chromatograph equipped with an HP 5921A atomic emission detector. Carbon, chlorine and bromine were monitored at wavelengths of 496, 479 and 478 nm, respectively. GC conditions: HP Ultra-1 column (50 m×0.32 mm, 0.17 μm phase thickness); carrier gas helium, at a flow-rate of 40 cm/s; split injection; injector temperature 250°C; temperature program, 50°C for 2 min, 10°C/min, 275°C for 5 min.

2.2.2. Py–GC–MS

Py–GC–MS analyses were carried out by using a Hewlett-Packard 5890 gas chromatograph equipped with an HP 5972 mass spectrometer and an HP-5 column (28.5 m×0.25 mm, 0.25 μm phase thickness), or a Shimadzu 14A gas chromatograph equipped with a QP-2000 mass spectrometer and an SGE BPX5 column (24 m×0.32 mm, 0.5 μm phase thickness). GC conditions as in Section 2.2.1.

2.3. Sampling and sample preparation

Bulk precipitation was sampled from individual rainfalls using open, funnel- or v-shaped, collectors (stainless steel; surface area 1–3 m^2, height 1.0–1.5 m). Precipitation samples were accumulated into 10-l glass bottles. Snow was collected by pushing 5-l polypropylene jars into snow packs of sufficient depth (20–40 cm) to avoid the snow that was close to the ground. The ambient temperature was below 0°C when snow was sampled.

Samples of organic matter for Py–GC analysis were prepared in two ways:

(i) the collected rainwater was rotary evaporated to dryness (water bath at 40°C);

(ii) solid-phase extraction of organic compounds was performed using a polyacrylate resin (XAD-8, Amberlite, Fluka), desorption with acetonitrile (for chromatography; Merck, Darmstadt, Germany), and evaporation of the acetonitrile eluate to dryness.

Information about sample types, sampling sites and enrichment methods is given in Table 1. The volume of the precipitation samples varied from 3 to

Table 1
Sample types, sampling sites and enrichment methods

Sample	Enrichment[a]	Sampling site	Site environment	Position	Sampling occasions
Snow	SPE	City of Gdansk, Poland	Densely built	54°22′N 18°35′E	March 1993
Rain	RE, SPE	Sobieszewo, (vicinity of Gdansk), Poland	Open land in built area	54°21′N 18°50′E	May 1996
Rain	RE	Königstein, (Frankfurt am Main), Germany	Open land in wooded area	50°11′N 08°30′E	October 1994
Rain	RE, SPE	City of Linköping, Sweden	Built	58°26′N 15°36′E	May 1995 and September 1996
Rain	RE	Glommen, Sweden	Open land	56°56′N 12°22′E	March, June and September 1995

[a] RE, rotary evaporation to dryness; SPE, solid-phase extraction.

5 l. The total yield of solids was in the order of 10 mg, and the amount pyrolysed in each run was less than 1 mg.

2.4. Experimental studies of the formation of chloroorganic compounds during pyrolysis

To study the formation of chloroorganic pyrolysis products by reactions between (non-chlorinated) organic matter and inorganic chloride present in the original samples, we performed pyrolysis experiments involving the stable isotope ^{35}Cl. Each of two rainwater samples collected at Glommen in southern Sweden were split into two aliquots. The first aliquot was evaporated to dryness without any additives. The second aliquot was evaporated after addition of sodium chloride enriched with respect to ^{35}Cl (>99% ^{35}Cl) (ORNL, Oak Ridge, TN, USA). The amount of ^{35}Cl added was either equal to or five times larger than the amount of chloride in the original sample. The solid residues of organic and inorganic matter obtained after evaporation to dryness were subjected to stepwise Py–GC–AED and Py–GC–MS.

To investigate whether chloroacetamides can be derived from reactions between ammonium and chloroacetic acids during pyrolysis, a solution of ammonium sulphate and chloroacetic acids was evaporated to dryness and then pyrolysed at 400°C.

3. Results

3.1. GC–MS analysis of major pyrolysis products

Py–GC–MS of organic matter enriched from rainwater showed that pyrolysis can render a great variety of organic moieties amenable to gas chromatographic analysis. When the pyrolysis temperature was 400°C, the TIC (total ion current) chromatograms displayed a large number of well resolved peaks (Fig. 1), and analysis in the full scan mode provided detailed information about the structure of the detected compounds. The compounds listed in Table 2 represent the major groups of pyrolysis products identified upon Py–GC–MS analysis of (i) solid residues of rainwater evaporated to dryness and (ii) organic compounds (in snow) enriched by adsorption to XAD-8, desorption with acetonitrile and evaporation of the eluate to dryness. Plausible precursors [5–7] of the identified pyrolysis products are also shown in Table 2. Apparently, pyrolysis of carbohydrates and nitrogen-containing biopolymers can explain a majority of the identified products, whereas pyrolysis of polyhydroxyaromatics seems to play a minor role. The detection of acetamide in the pyrolysate of rainwater evaporated to dryness indicates the presence of amino sugars in the original sample. In addition to the listed compounds, several nitrophenols of unknown origin were detected in both types of samples.
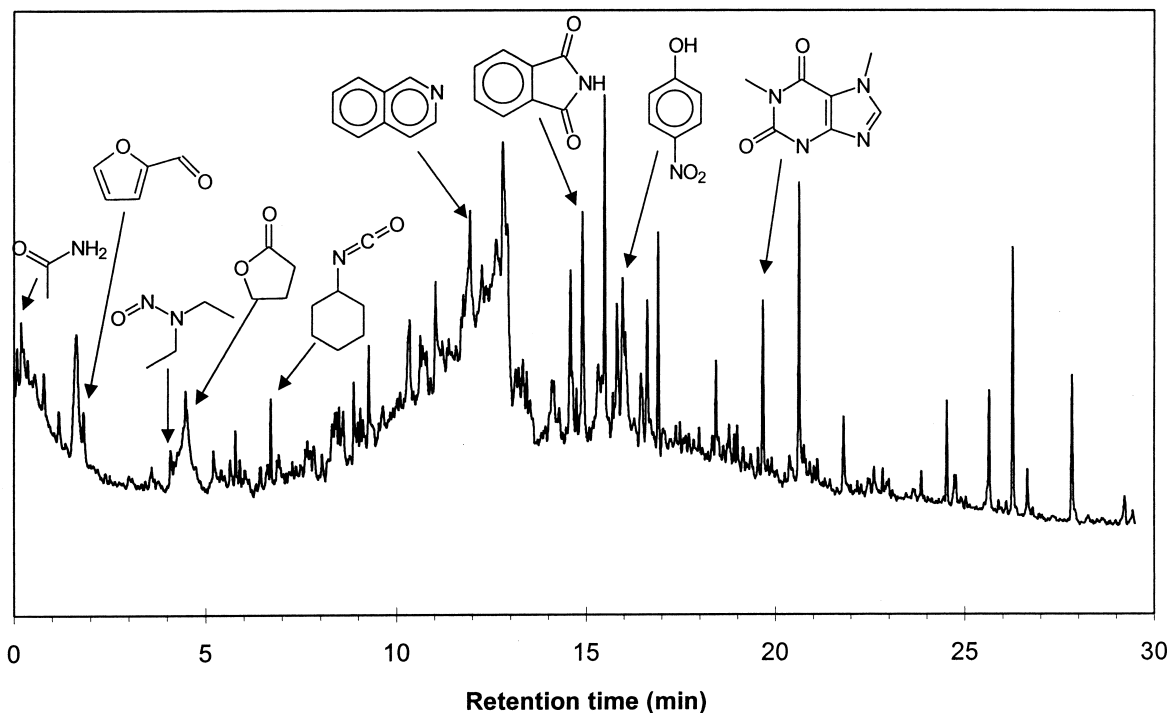
Fig. 1. TIC (total ion current) chromatogram recorded during Py–GC–MS analysis of residues of a rainwater sample evaporated to dryness. The rainwater was collected at Königstein in Germany. The pyrolysis temperature was 400°C.

3.2. GC–AED analysis of halogenated pyrolysis products

3.2.1. Isothermal pyrolysis at 400°C

When organic matter enriched from precipitation was analysed by Py–GC–AED, the chromatograms recorded in the chlorine channel (479 nm) had the following characteristics: a large peak followed by a cluster of small peaks in the retention time interval 2–5 min; a sizable hump in the middle of the chromatogram; and few or no peaks after the large hump (Fig. 2). Examination of so-called snapshots of emission line spectra confirmed that the major peaks were caused by chlorinated compounds. The hump was caused by formation of HCl during the pyrolysis. Due to the presence of interfering compounds (e.g. water and amines) in the pyrolysates the retention time of HCl varied from sample to sample. The identification of HCl was based on the response to chlorine and hydrogen in the GC–AED system and on GC–MS analysis in the full scan mode.

3.2.2. Stepwise pyrolysis

The formation of volatile chlorinated pyrolysis products was further investigated by first heating samples of organic compounds enriched from precipitation to a temperature of 150°C and then sequentially pyrolysing the same samples at 400, 600 and 750°C. The chromatograms in Fig. 3 demonstrate that the previously mentioned peaks in the retention time interval from 2 to 5 min appeared after pyrolysis at 400°C. Thermal desorption of volatiles at 150°C did not produce any peaks in the indicated interval, and the pyrolysis products detected at 600 and 750°C were also formed at 400°C. The chromatograms in Fig. 3 refer to a sample collected at Königstein in Germany; similar results were obtained for rainwater samples collected at Glommen and Linköping in southern Sweden.

3.3. GC–MS identification of chlorinated pyrolysis products

The structures of the chlorinated compounds de-

Table 2
Major pyrolysis products of organic matter in precipitation and plausible parent compounds of the identified products

Plausible parent compounds	Pyrolysis products of	
	Solid residues of rainwater evaporated to dryness	Organic compounds enriched from melted snow by solid-phase extraction
Carbohydrates	2-Furancarboxaldehyde (furfural)	Cyclopentenone
	Dihydro-2(3H)-furanone	2-Furancarboxaldehyde (furfural)
	Furan	Dihydro-3-methylene-2,5-furandione
	5-Methyl-2-furancarboxaldehyde	2-Methyl-2-cyclopenten-1-one
		1-(2-Furonyl)-ethanone
		Dihydro-5-methyl-2[3H]-furanone
		3-Methyl-2-cyclopenten-1-one
		Cyclopentanone
		Tetrahydro-6-methyl-2H-pyran-2-one
		5-Butyldihydro-2(3H)-furanone
		4-Methyl-1,3-isobenzofuranone
Polyhydroxy aromatic compounds		Phenol
		2-Methyl-phenol
Proteins, peptides, chitin	Hexanenitrile	Isopropylnitrile
	N-Ethyl-N-nitrosoethanamine	Pyridine
	Cyclohexylisocyanate	Pyrrole
	1H-Pyrrole-2-carboxaldehyde	2-Methylpyridine
	4-Nitrosomorpholine	2-Methyl-1H-pyrrole
	Isoquinoline	Hexanenitrile
	1H-Isoindole-1,3(2H)-dione	1H-Isoindole-1,3(2H)-dione
	2H,4H-1,3-Isoquinolinedione	
	Caffeine	
Amino sugars	Acetamide	

Compounds listed were obtained from the residues of a rainwater sample (Königstein, Germany) evaporated to dryness and organic compounds enriched from melted snow (Gdansk, Poland) by adsorption on XAD-8 followed by desorption with acetonitrile. The pyrolysis temperature was 400°C.
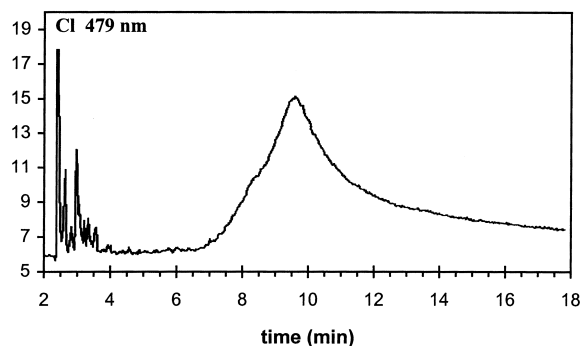

Fig. 2. Py–GC–AED analysis of organic substances enriched by evaporating rainwater to dryness. The chromatogram shows the response in the chlorine channel (479 nm), and the pyrolysis temperature was 400°C. The rainwater was collected at Glommen, southern Sweden.

tected in the Py–GC–AED runs were investigated by Py–GC–MS analysis of the same samples. The compounds identified and the information that led to their identification are described below. The structures are depicted in Fig. 4.

3.3.1. Chloromethane

The largest peak in the chromatograms recorded in the chlorine channel of the GC–AED system was caused by a chlorine-containing compound that was not retarded by interaction with the stationary phase of the GC column. Chloromethane exhibits such a property, and GC–MS analysis showed that the mass fragments characteristic of that compound (i.e. m/z 50, 52 and 15) appeared at the same retention time as carbon dioxide and water. Plausible reactions responsible for the formation of chloromethane are dis-
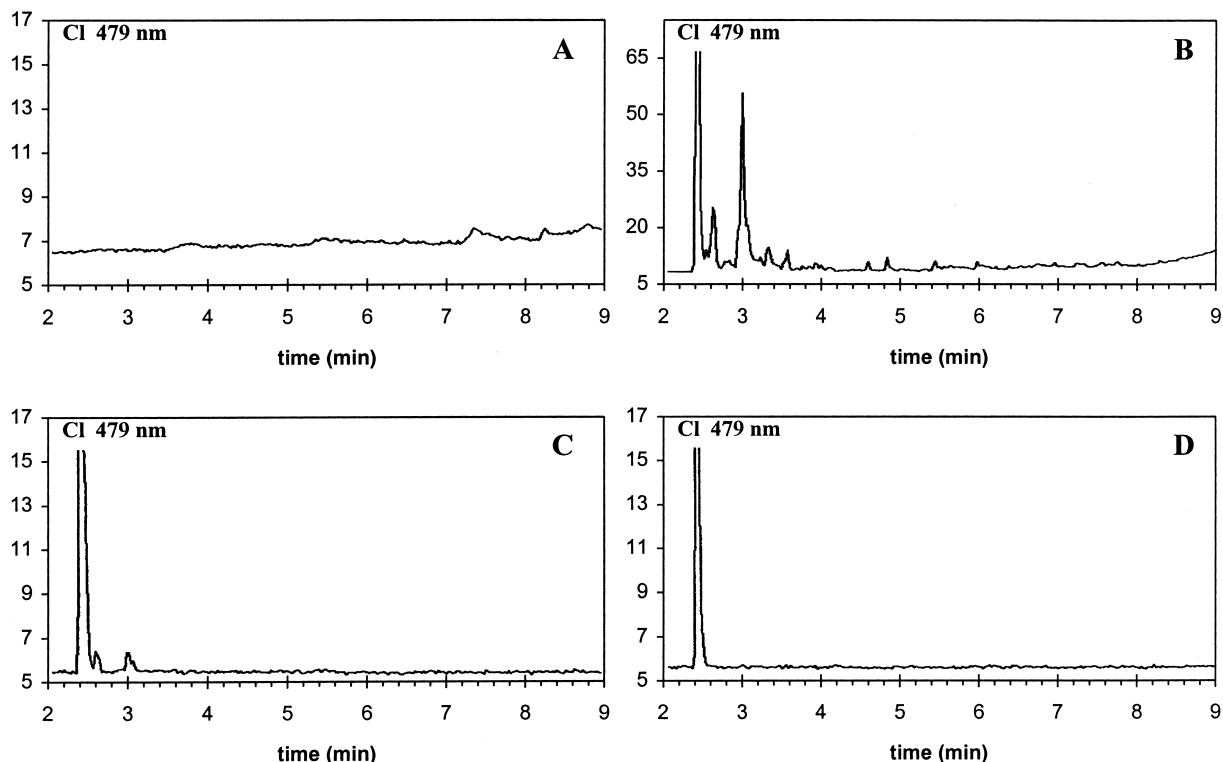
Fig. 3. Stepwise Py–GC–AED analysis of solid residues obtained by evaporating rainwater to dryness. The four chromatograms show the response in the chlorine channel (479 nm) after thermal desorption at 150°C (A) and pyrolysis at 400°C (B), 600°C (C) and 750°C (D). The rainwater was sampled at Königstein in Germany. Note a different scale of *y* axis in (B).
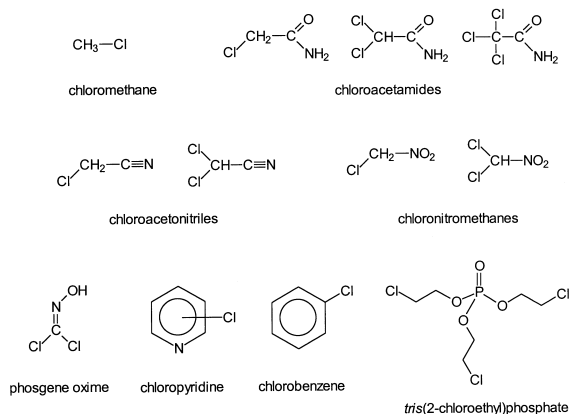

Fig. 4. Chemical structures of chloroorganic compounds identified in pyrolysates of organic compounds enriched from precipitation.

cussed in the section concerning isotope experiments.

3.3.2. Chloroacetamides

Compounds with mass spectra almost identical to the library spectra of mono-, di- and trichloroacetamide were present in significant amounts in some of the analysed samples. Di- and trichloroacetamide were actually responsible for two of the major peaks in a chromatogram obtained by GC–MS analysis of organic compounds derived from rainwater collected at Glommen in southern Sweden. The identity of the detected compounds was confirmed by using the Py–GC–AED and Py–GC–MS systems to thermally desorb (150°C) and analyse reference samples of mono-, di- and trichloroacetamide.

3.3.3. Nitrogen-containing chloroorganic compounds other than chloroacetamides

In addition to chloroacetamides, several other nitrogen-containing chloroorganic compounds were detected in the analysed samples. Thorough evaluation of mass spectra provided strong evidence that mono- and dichloroacetonitrile, phosgene oxime and two isomers of chloropyridine can occur in pyrolysates of organic compounds enriched from precipitation. Furthermore, mono- and dichloronitromethane were tentatively identified.

3.3.4. Chlorobenzenes

A search for chlorobenzenes in the samples analysed by GC–MS revealed that monochlorobenzene was present in the pyrolysate of organic compounds derived from rainwater collected at Glommen.

3.3.5. Chloroalkylphosphates

The compound tris(2-chloroethyl)phosphate was detected after thermal desorption (150°C) of organic compounds enriched by solid-phase extraction of snow collected in Gdansk and rainwater collected at Sobieszewo in Poland and in Linköping, Sweden.

3.4. Experimental studies of the formation of chloroorganic compounds during pyrolysis

The results of the ^{35}Cl studies are summarised in Table 3. Although the relative abundance of ions detected by GC–MS displayed some irregular variation, the general pattern in observed data was clear. When pyrolysis was carried out in the presence of inorganic chloride enriched with regard to ^{35}Cl, a surplus of ^{35}Cl was found in the chloroorganic pyrolysis products, which indicates that reactions involving inorganic chloride contributed to the presence of chloroorganic compounds in the analysed pyrolysates. Closer examination of the relative abundance of mass fragments containing ^{35}Cl and ^{37}Cl, respectively, showed that ^{35}Cl was normally more abundant in such fragments than in natural chlorine isotopic composition, but less abundant than would have occurred if reactions involving inorganic chloride had been the only source of the chloroorganic compounds in the pyrolysate.

Chloromethane provides an example of a chloroorganic pyrolysis product that was probably formed mainly in reactions between inorganic chlorine species and non-chlorinated organic matter. Table 3 shows that the intensity ratio of ions 52 and 50

Table 3
Relative abundance of different chlorine-containing ions detected by Py–GC–MS analysis of samples pyrolysed with or without the addition of sodium chloride enriched with respect to ^{35}Cl (>99%)

Compound	Ions (m/z)	Natural ratio ^{37}Cl/^{35}Cl	Observed (expected) relative abundance ratios of ions containing ^{37}Cl or ^{35}Cl	
			No additives	Addition of inorganic ^{35}Cl[a]
Chloromethane	50, 52	0.32	0.36	0.07 (0.04)[b]
Monochloroacetonitrile	48, 50	0.32	0.28	0.03 (0.04)[b]
	75, 77	0.32	0.30	0.04 (0.04)[b]
Chloropyridine	113, 115	0.32	0.29	0.06 (0.04)[b]
Chlorobenzene	112, 114	0.32	0.33	0.08 (0.04)[b]
Phosgene oxime	78, 80	0.32	0.32	0.20 (0.14)[c]
	61, 63	0.32	0.38	0.24 (0.14)
	113, 115	0.64	0.68	0.37 (0.28)
	113, 117	0.10	0.11	0.030 (0.002)
Monochloroacetamide	93, 95	0.32	0.34	0.22 (0.14)[c]
	49, 51	0.32	0.38	0.16 (0.14)

[a] Values given within parentheses show the relative abundance that could be expected if 100% of the chloroorganic compounds under consideration originated from reactions involving inorganic, ^{35}Cl-enriched chloride.
[b] Large, amount of ^{35}Cl added was five times the amount of chloride in the sample.
[c] Moderate, amount of ^{35}Cl added was equal to the amount of chloride in the sample.

decreased significantly when [35]Cl was added to the sample as chloride. Moreover, it is well known that both HCl and CH_3OH can be released from organic matter and that the two compounds can react to form chloromethane and water [10]. The results regarding chloroacetonitrile were also straightforward in the sense that addition of [35]Cl as inorganic chloride clearly altered the relative intensity of the chlorine-containing fragments. On the other hand, the low intensity of such fragments in the observed mass spectra of dichloroacetonitrile made it more difficult to draw precise conclusions regarding this compound.

The mass spectra of phosgene oxime shown in Fig. 5 further indicate how addition of [35]Cl as chloride changed the isotope composition of chloro-organic pyrolysis products. Mono- and dichloronitromethane, chloropyridine and chlorobenzene provide yet other examples of chloroorganic compounds that may be formed during pyrolysis due to reactions between inorganic chloride species and non-chlorinated organic compounds.

The results regarding monochloroacetamide were not fully conclusive. The relative abundance of ions containing [37]Cl decreased when the pyrolysis was undertaken with a surplus of [35]Cl as inorganic chloride. However, the intensity ratios of [35]Cl and [37]Cl were not identical in the two chlorine-containing fragments (*m/z* 51 and 49, and *m/z* 95 and 93). Moreover, it is worth noticing that no chloroacetamides were formed when a concentrate of

chloroacetates and ammonium sulphate was pyrolysed. The results regarding di- and trichloroacetamide were uncertain due to the low intensity of the chlorine-containing fragments in mass spectra.

4. Discussion

Pyrolysis followed by GC–MS or GC–AED detection was found to be an interesting complement to more conventional analytical procedures for organic compounds in rain and snow. The merits of the investigated technique were obvious. A substantial fraction of the organic compounds present in precipitation was sufficiently non-volatile to be enriched by evaporation of the original sample or an extract thereof, and the pyrolysates of the solid residues thus obtained chromatographed well. The conditions for identification of pyrolysis products were satisfactory also in other respects: the yield of a great variety of compounds was high enough to enable both element-specific detection, using a GC–AED system, and mass spectrometric detection in the full scan mode. The major pyrolysis products listed in Table 2 can be regarded as an illustration of the power of the technique. If desired, a substantially longer list of pyrolysis products can be fairly easily obtained.

The weak point of the investigated analytical procedure, and of all pyrolysis techniques, is the unclear relationship between pyrolysis products and
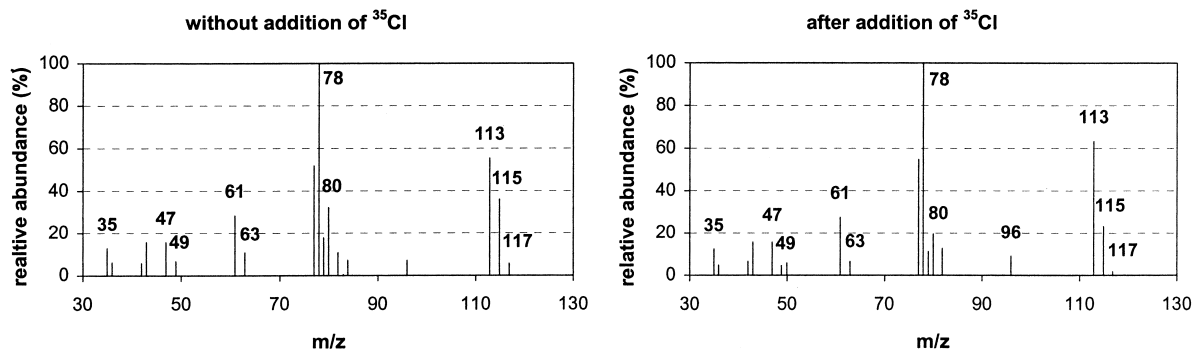

Fig. 5. Mass spectra of phosgene oxime recorded upon Py–GC–MS analysis of rainwater evaporated to dryness. Addition of [35]Cl-enriched chloride in an amount equal to five times the original chloride content of the sample. The rainwater was collected at Glommen, southern Sweden. Observed and expected ion ratios for the fragments *m/z* 61, 63; 78, 80; 113, 115, 117 are shown in Table 3.

precursors. There are three major reasons for this uncertainty:

(i) pyrolysis is often employed to analyse very complex molecules;

(ii) information about pyrolysis products of specific compounds is often scarce;

(iii) organic structures that were not present in the original samples can be formed during pyrolysis.

The first reason for the unclear relationship is a direct consequence of the complexity of the problems addressed; the second explanation can gradually be removed by systematic efforts, i.e. the more pyrolysis is used to investigate complex mixtures of organic matter, the more powerful the technique will be. The third reason, i.e. pyrolytic artefacts, was found to be particularly important when analysing chloroorganic compounds in precipitation. The ^{35}Cl experiments provided clear evidence that at least a part of the low-molecular-mass chloroorganic compounds detected in the pyrolysates were formed by reactions between organic compounds released from the sample and reactive chlorine derived from inorganic chloride. Studies of biomass combustion have provided detailed knowledge about the formation of chloromethane through reactions between CH_3OH and HCl [10], and the cited article also provides general information about the formation of chlorine radicals. Reacting methanol with HCl at elevated temperatures has even been utilised for industrial production of chloromethane [10].

Our experiments with ^{35}Cl also showed that the isotope distribution of the chlorine detected in several of the pyrolysis products was somewhere between that of the inorganic chloride enriched with respect to ^{35}Cl and the natural distribution prevailing in organic matter enriched from precipitation. This indicates that at least a part of the moieties of some of the detected and identified chloroorganic compounds were present in the organic matter subjected to pyrolysis. However, the results were not entirely conclusive. First, there was some uncertainty regarding quantification of the isotope ratios. Second, it cannot be excluded that reactive chlorine derived from the organic matter present in the samples played a significant role. Further studies, in which almost all inorganic chloride is removed from a precipitation sample prior to pyrolysis might shed new light on the origin of low-molecular-mass chlorinated pyrolysis products of organic matter derived from precipitation.

5. Conclusions

Pyrolysis rendered a great variety of organic substances in rainwater amenable to GC analysis.

Py–GC–MS analyses revealed that the major groups of pyrolysis products were nitrogen-containing and cyclic-oxygen-containing compounds, which indicates the presence of biopolymers, such as carbohydrates, proteins, peptides and chitin, in the analysed precipitation samples.

Py–GC–AED and Py–GC–MS analyses showed that tris(2-chloroethyl)phosphate was thermally desorbed from solid residues of precipitation and organic extracts thereof, and that several low-molecular-mass chloroorganic compounds, such as chloromethane and chlorinated acetamides, acetonitriles, and nitromethanes, were formed during the pyrolysis.

Isotope experiments revealed that the low-molecular-mass chlorinated pyrolysis products detected in the pyrolysates were, at least in part, formed through reactions between organic compounds released from the sample and reactive chlorine derived from inorganic chloride.

Acknowledgements

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