

# Analysis of Polystyrene in Polluted Sediments by Pyrolysis–Gas Chromatography–Mass Spectrometry

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## Abstract

The use of pyrolysis combined with gas chromatography and mass spectrometry for the analysis of polystyrene in sediments is described. The method is applied to a sediment core of the Lagoon of Ravenna (Pialassa Baiona); in these sediments, polystyrene is detected at mg/g levels in surface layers. Dried sediment samples are directly pyrolyzed in a quartz tube holder, the peak area of the evolved styrene is determined in the single ion monitoring mode, and polystyrene concentration is calculated from the appropriate calibration curve. Linear plots of styrene peak area versus polystyrene content are obtained by pyrolyzing the polymer in the presence of various matrices: calcite, quartz, kaolinite, montmorillonite, and whole sediment. The pyrolytic behavior of polystyrene is strongly affected by the presence of clay minerals, whereas calcite and quartz exhibit a lower influence. The effect of other organic constituents, such as humic substances and styrene-butadiene rubbers, is discussed.

## Introduction

Polystyrene is a thermoplastic material largely utilized in industrial and domestic settings for many applications, such as packaging, consumer products, disposable serveware, electronic devices, and furnishings. The careless disposal of domestic and industrial wastes leads to its occurrence in marine (1–2) and terrestrial environments (3). Recently, polystyrene has been identified as a significant organic pollutant in sediments of Pialassa Baiona (4). Pialassa Baiona is a wetland connected to the Adriatic Sea and located in proximity of the city of Ravenna, Italy. Its sediments have been heavily contaminated by mercury from the industrial wastes of nearby chemical plants (4–6).

The identification of polystyrene has been accomplished

using pyrolysis coupled with gas chromatography and mass spectrometry (pyrolysis–GC–MS), and preliminary data have showed a strong correlation between polystyrene and mercury concentration (4). The potential of analytical pyrolysis for the detection of organic pollutants, including polystyrene, in soils and sediments is known (3,7). However, even though analytical pyrolysis has been used for quantitative analyses of polystyrene in different materials, such as acrylic plastics (8) and explosives (9), there are no reports in the literature dealing with its quantitation in sediments.

A procedure for the determination of the polystyrene concentration in sediments using pyrolysis–GC–MS is proposed. For this purpose, emphasis is put on determining the effect of inorganic matrices on the results generated by this technique.

## Experimental

Calcite and quartz were obtained from Carlo Erba. Polystyrene was obtained from Aldrich (Milwaukee, WI). Kaolinite was obtained from Dorfner (Hirschau, Germany). Montmorillonite was obtained from Laviosa (Livorno, Italy). The sediment core was collected in April 1995 in a channel of the southern part of Pialassa Baiona (4). The content of carbonates was obtained by volumetric determination of the evolved carbon dioxide after treatment with 10% HCl. The separation of grain-size fractions was carried out by wet sieving. The identification of minerals was performed using a Philips (Almelo, The Netherlands) PV 1840 X-ray diffractometer. All solid samples were dried at 105°C.

Samples were pyrolyzed in a quartz holder at 700°C (set temperature) for 10 s at the maximum heating rate using a CDS (Oxford, PA) 1000 pyroprobe heated filament pyrolyzer connected to a Varian (Palo Alto, CA) 3400 GC and a Saturn (Varian) II ion-trap MS. The pyrolysis–GC interface and split-splitless injector were kept at 250°C. The carrier gas was

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helium at 1.0 mL/min. The injector mode was split with a 1:60 split/splitless ratio. The separation of the pyrolysis products was carried out using a J&W Scientific (Folsom, CA) DB-5MS fused-silica capillary column (30 m  $\times$  0.25 mm, 0.25- $\mu$ m film thickness, 5% phenyl-95% methylsiloxane). The column temperature was held at 50°C for 2 min and programmed to a final temperature of 300°C at 15°C/min. Mass spectra were recorded under electron impact (70 eV) at 1 scan/s in the mass range  $m/z$  45–350. Peak areas were calculated in the selected ion monitoring (SIM) mode using the molecular ion and the base peak as target ions.

Approximately 10 mg of solid sample was inserted into the central part of the quartz tube, where the highest temperature is attained. Then, 5  $\mu$ L of polystyrene solution was spread evenly into the solid, which was pyrolyzed after evaporation of the solvent. Polystyrene solutions were prepared in dichloromethane at various concentrations by diluting a standard solution (100 mg polystyrene in 25 mL solution).

## Results and Discussion

### Pyrolysis-GC-MS of polystyrene

The pyrolytic behavior of polystyrene in the presence of calcite, quartz, kaolinite, and montmorillonite was investigated. These are ubiquitous minerals encountered in sediments. Kaolinite is a 1:1-type clay mineral with stacked layers composed of tetrahedral silica and octahedral aluminum hydroxide sheets. Montmorillonite is a 2:1-type clay mineral whose unit layer structure consists of an octahedral aluminum hydroxide sheet between two tetrahedral silica sheets. Kaolinite is a non-expanding clay with a small ion-exchange capacity, whereas montmorillonite is an expanding clay with a large ion-exchange capacity and large specific surface area.

Figure 1 shows the total ion chromatograms obtained by pyrolyzing polystyrene in the presence of calcite and quartz. Pyrograms obtained in the presence of kaolinite and mont-

morillonite are depicted in Figure 2. The principal pyrolysis products identified in the pyrograms and their relative abundances are reported in Table I. The relative abundance of each compound is its peak area expressed as a percentage of the total peak area resulting from all the compounds listed in Table I. Replicate measurements produce relative standard deviations in the 1–15% range for the most intense peaks.

The data in Table I show that the product distribution obtained after pyrolysis of polystyrene in the presence of calcite is similar to that observed in the presence of quartz. Styrene is by far the predominant thermal degradation product (90% of total area), followed by styrene dimer (2,4-diphenyl-1-butene), bibenzyl (1,2-diphenylethane), toluene, 1,2-diphenylpropane, and  $\alpha$ -methylstyrene (2-phenylpropene). Pyrolysis of neat polystyrene yields mostly styrene monomer, followed by styrene oligomers (mainly dimer and trimer) (10,11). Styrene is produced through the depolymerization of macroradicals formed by random thermal cleavage of the main chain, whereas styrene dimer is thought to be formed by intermolecular reactions (11). Benzene, toluene, ethylbenzene, styrene,  $\alpha$ -methylstyrene, bibenzyl, and 1,2-diphenylpropane have been also detected as thermal degradation products of neat polystyrene (10,12).

When pyrolyses of polystyrene are performed in the presence of clay minerals, important changes in the product distribution are noticeable (Figure 2 and Table I). Styrene remains the predominant pyrolysis product in the presence of kaolinite, but its relative abundance decreases from 90% (calcite, quartz) to 70%, and benzene

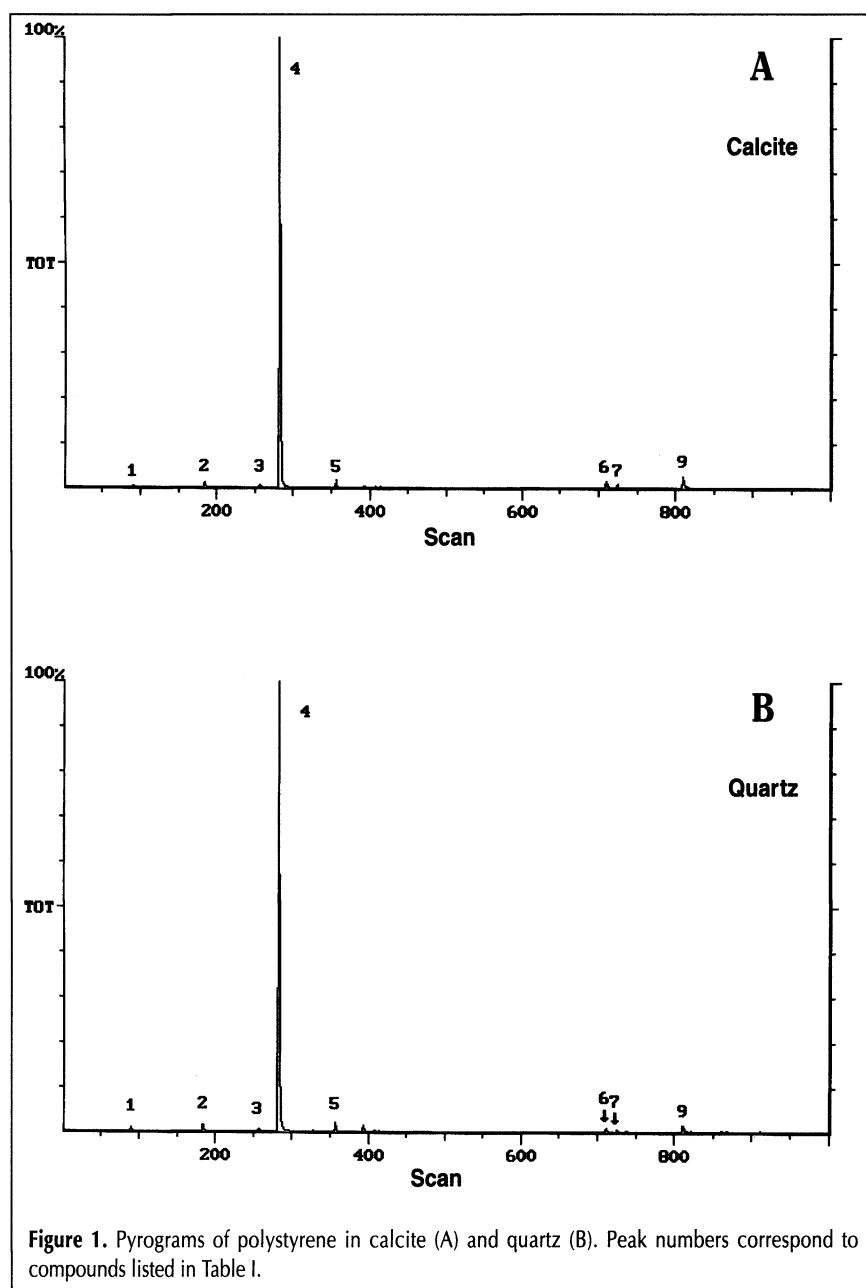


Figure 1. Pyrograms of polystyrene in calcite (A) and quartz (B). Peak numbers correspond to compounds listed in Table I.

**Table I. Product Distribution (% of Total Peak Area) Obtained After Pyrolysis–GC–MS of Polystyrene (15 µg) in Various Inorganic Matrices**

| Number | Product             | Quantitation mass<br>(base peak + molecular ion) | Matrix  |        |           |                 |
|--------|---------------------|--|---------|--------|-----------|-----------------|
|        |                     |  | Calcite | Quartz | Kaolinite | Montmorillonite |
| 1      | Benzene             | 78   | 0.4     | 0.4    | 10.8      | 67.5            |
| 2      | Toluene             | 91 + 92  | 2.0     | 3.1    | 4.4       | 5.2             |
| 3      | Ethylbenzene        | 91 + 106   | 0.69    | 0.80   | 2.2       | 12.8            |
| 4      | Styrene             | 104  | 90.2    | 90.9   | 70.0      | 11.8            |
| 5      | α-Methylstyrene     | 117 + 118  | 1.3     | 1.5    | 9.4       | 1.6             |
| 6      | Bibenzyl            | 91 + 182   | 2.1     | 1.4    | 0.4       | 0.2             |
| 7      | 1,2-Diphenylpropane | 105 + 196  | 0.7     | 0.5    | 0.1       | 0.2             |
| 8      | 1,2-Diphenylpropene | 194  | —*      | —*     | 2.3       | 0.4             |
| 9      | Styrene dimer       | 91 + 208   | 2.4     | 1.5    | 0.4       | 0.3             |

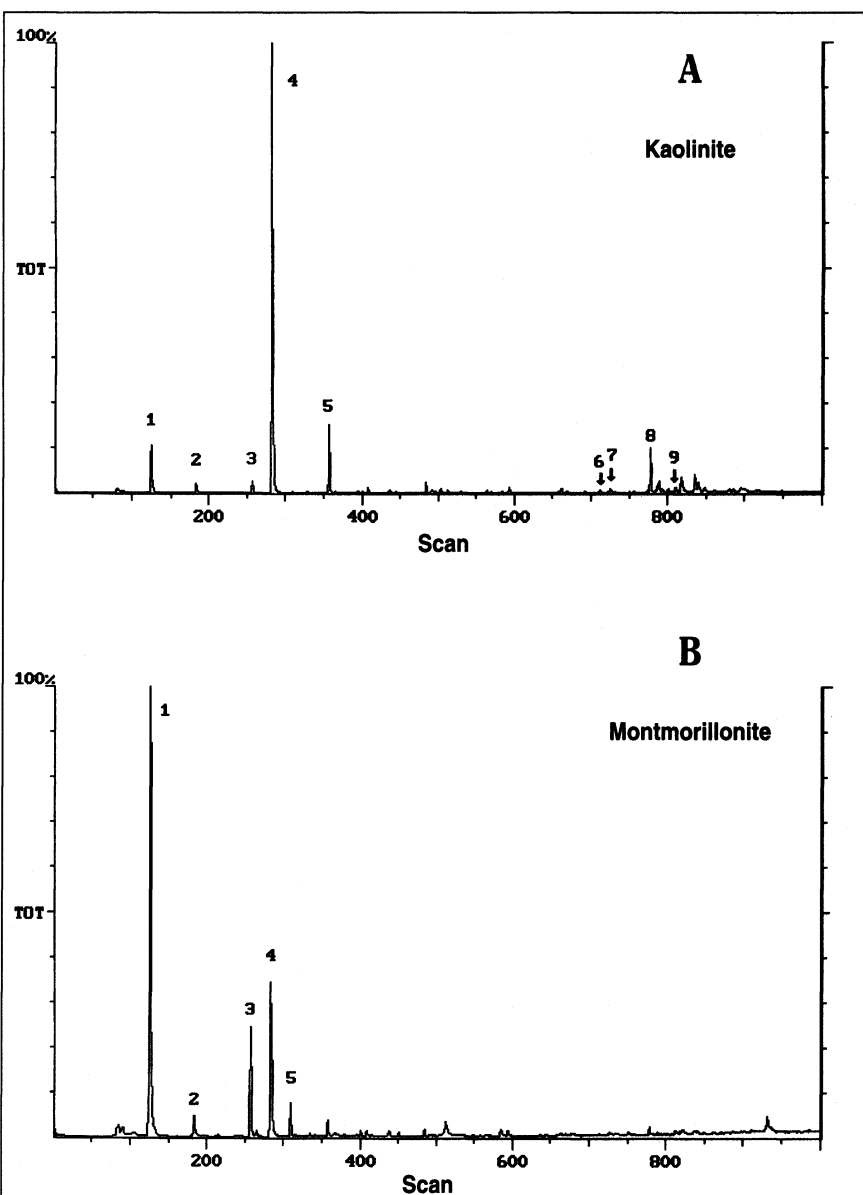
\* Less than 0.1%.

and α-methylstyrene increase up to 10%. Diphenylpropene is a primary pyrolysis product at high retention times. This compound has been detected in pyrolysates of head-to-head polystyrene (10). The thermal behavior of polystyrene is deeply affected by montmorillonite. In this clay, benzene becomes the predominant pyrolysis product (67%), and the relative content of styrene drops to 12% (a value similar to that of ethylbenzene).

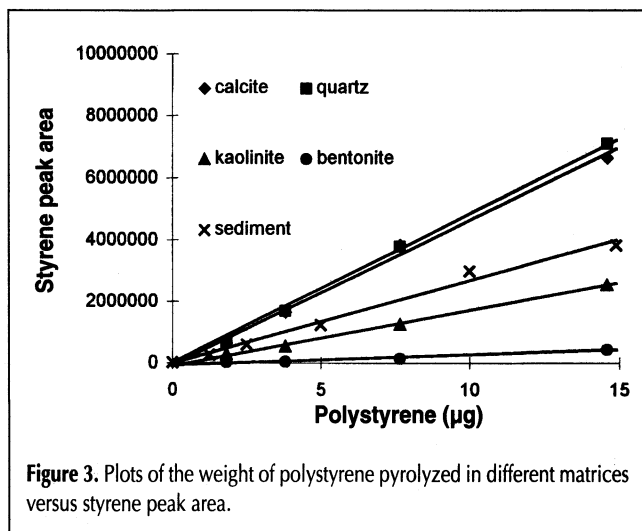
Calibration curves of the four minerals are constructed by plotting the peak area of styrene released after pyrolysis against the amount of added polystyrene (Figure 3). Linear relationships are observed for all the minerals (correlation coefficient  $r > 0.99$ ), but the slope of the curves decreases in the following order: calcite/quartz, kaolinite, montmorillonite. These differences are attributed to the different efficiency of styrene formation in the various matrices.

#### Pyrolysis–GC–MS of sediments

Pyrolysis–GC–MS was applied to a sediment core collected in a polluted site of Pialassa Baiona (4). A brief description of the sediment samples is reported in Table II. Pyrograms obtained after direct pyrolysis of a few milligrams of sediment samples reveal the occurrence of polystyrene in samples 1 and 2 (Figure 4). The identification is based on the high levels of styrene, which is the most intense peak, and the presence of polystyrene markers such as bibenzyl and styrene dimer. The presence of polystyrene in sediments of this area has been confirmed by pyrolysis–GC–MS and  $^{13}\text{C}$ -nuclear magnetic resonance analyses on the organic residue remaining after the elimination of



**Figure 2.** Pyrograms of polystyrene in kaolinite (A) and montmorillonite (B). Peak numbers correspond to compounds listed in Table I.



extractable humic substances on a surface sediment (13).

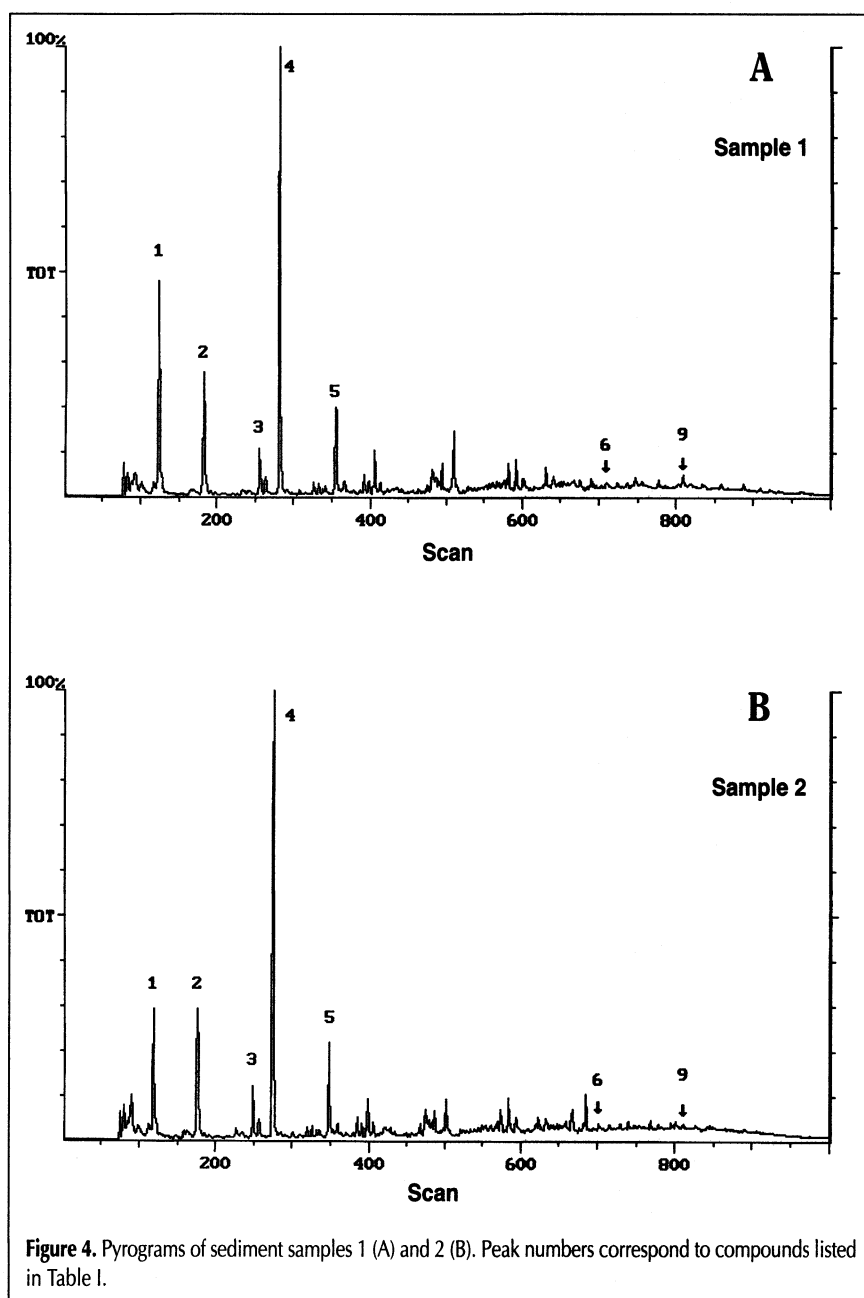
Because styrene yields are influenced by the presence of inorganic components, calibration plots for calculating polystyrene concentrations are constructed in a solid matrix as similar as possible to the analyzed samples. This is accomplished by using sediment samples belonging to uncontaminated portions of the same core. The low values of mercury concentrations (Table II) make samples 4 and 5 adequate standard matrices for the construction of the calibration curve. According to X-ray diffraction spectra, all samples exhibit a qualitatively similar mineral composition, with quartz and calcite being the dominant minerals and chlorite, illite, smectite, and kaolinite being the principal clay minerals in fine fractions. Carbonate contents are also similar, and the relative content of the fine fraction (silt and clay) increases with increasing depth.

Figure 3 shows the calibration curve obtained by pyrolyzing polystyrene in the presence of sediment sample 4. The plot of the

styrene peak area versus the amount of added polystyrene yields a straight line with a correlation coefficient  $r$  of 0.992. A linear calibration plot is also observed using the peak area  $\alpha$ -methylstyrene ( $r = 0.996$ ), so that this marker can be used in place of styrene. The reproducibility of peak area, tested with four consecutive runs of 10  $\mu\text{g}$  added polystyrene, is 2% for styrene and 9% for  $\alpha$ -methylstyrene. Concentrations of polystyrene in sediment samples are reported in Table II. Polystyrene mostly occurs in the top 20 cm of the sediment core at a concentration of 3–4 mg/g, corresponding to 10–20% of the total organic carbon.

In addition to inorganic phases, organic components may also influence the reported results. In fact, styrene is a thermal degradation product of natural organic matter, principally humic substances (13–15). Pyrolysis–GC–MS analyses of humins and humic acids, the most abundant organic components in soils and sediments, have shown that toluene is the most abundant pyrolysis product and the styrene/toluene peak-area ratio occurs in the 0.1–0.4 range (13). The value of the styrene-to-toluene ratio is 0.2 in samples 4 and 5 (suggesting that pyrolysis products derive mainly from humic matter) and 1.4 and 1.7 in samples 1 and 2, respectively (indicating that polystyrene is the dominant precursor of styrene). In the case of sediment sample 4, the peak area of sediment-derived styrene corresponds to 0.01  $\mu\text{g}$  polystyrene per milligram sediment. These findings seem to indicate that humic substances do not represent a serious interference in samples with polystyrene contents as high as those exhibited in the present study.

Polybutadiene, acrylonitrile-butadiene-



**Table II. Chemical Data of a Sediment Core Taken from Pialassa Baiona**

| Sample | Depth (cm) | Carbonate (%) | Texture* (% fine fraction) | TOC (%) | Hg* ( $\mu\text{g/g}$ ) | Polystyrene (mg/g) |
|--------|------------|---------------|----------------------------|---------|-------------------------|--------------------|
| 1      | 0–10       | 24            | 44                         | 1.6     | 57                      | 3.3                |
| 2      | 10–20      | 26            | 57                         | 3.5     | 244                     | 3.9                |
| 3      | 20–30      | 28            | 74                         | 1.2     | 28                      | 0.1                |
| 4      | 30–40      | 28            | 80                         | < 1     | 0.42                    | —                  |
| 5      | 40–50      | 27            | 83                         | < 1     | 0.17                    | —                  |

\* Data from reference 4.

## References

styrene (ABS), random styrene-butadiene (SBR), and block styrene-butadiene (SBS) copolymers have been produced by chemical plants in the industrial area near Pialassa Baiona. Among them, ABS, SBS, and SBR yield styrene and  $\alpha$ -methylstyrene upon pyrolysis. SBR is identified in sediment samples 1 and 2 by the presence in the pyrograms of trace levels of styrene-butadiene, a characteristic pyrolysis product of SBR (16–17). Butadiene, butadiene dimer, and butadiene trimers are thermal degradation products originating from the polybutadiene portion of SBR. However, the peak areas of butadiene markers relative to styrene are too small to be used as a measurement of the contribution of SBR in these sediments.

Styrene yields from polystyrene are dependent on such other factors as the molecular weight of polystyrene (12), the presence of humic materials (15), and experimental parameters (18). Attempts to compare the polystyrene content determined using pyrolysis–GC–MS with the use of alternative techniques, such as infrared spectroscopy, failed because of the difficulties encountered in quantitatively extracting polystyrene from the mineral matrix. In this case, the capability of analytical pyrolysis to directly analyze the whole sediment is advantageous.

## Conclusion

Pyrolysis–GC–MS is a valid technique for the identification and quantitative estimation of polystyrene in polluted sediments. The method is simple and rapid because no sample treatment is required other than drying and milling. The use of SIM is particularly useful for the integration of chromatographic peaks obtained from pyrolysis of sediments, which produces a large amount of overlapping peaks originating from adsorbed organic matter.

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