

Direct Determination of Styrene and Tetrachloroethylene in Olive Oil by Membrane Inlet Mass Spectrometry

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A rapid screening method of styrene and tetrachloroethylene in olive oil based on membrane inlet mass spectrometry has been developed. The presence of these contaminants was identified and monitored on the basis of the mass spectra measured. Detection limits of 100 and 5 ppb were measured for styrene and tetrachloroethylene, respectively. A linear dynamic range of at least 3 orders magnitude was achieved. Fast response times, in the order of 1 min, for the analytes were observed, allowing large sample throughput.

Keywords: Olive oil; membrane inlet mass spectrometry; tetrachloroethylene; styrene; solvent analysis

INTRODUCTION

Olive oil can be contaminated by organic solvents during storage or during production. One particular example is contamination by styrene (Nerin et al., 1993). This can happen when olive oil is stored in containers made out of polymers containing large amounts of styrene monomer, such as polystyrene or acrylonitrile-butadiene-styrene (ABS). Another likely contaminant is tetrachloroethylene (Norman, 1991; Pocklington, 1992). Contamination of olive oil by tetrachloroethylene has been attributed to the accidental tetrachloroethylene spills occurring during the oil content measurement of crushed olives (Pocklington, 1992). Due to the toxicity of these possible contaminants, their concentrations in food (Nerin et al., 1993) and olive oil (Norman, 1991; Pocklington, 1992) are regulated within the European Union, and several analytical methods have been developed to analyze such compounds in olive oil. A commonly used method is head space gas chromatography (Norman, 1991; Pocklington, 1992; Nerin et al., 1993). The drawback of this and other conventional methods is that they can be time consuming.

In this study, membrane inlet mass spectrometry (MIMS) (Kotiaho et al., 1991; Degn, 1992; Lauritsen and Lloyd, 1994) was used for direct analysis of styrene and tetrachloroethylene in olive oil. Membrane inlet mass spectrometry is an analytical technique in which a polymer membrane is used as the only interface between the liquid sample, in this case the olive oil, and a mass spectrometer. Volatile organic compounds penetrate the membrane and evaporate into the vacuum of the mass spectrometer, where they are ionized and analyzed. The olive oil on the other hand passes the nonporous silicone membrane only in minor quantities. The main advantages of MIMS as an rapid on-line analytical technique are as follows: (i) volatile organic compounds can be measured directly without any sample treatment from solution at parts per billion (ppb) and parts per trillion (ppt) levels; (ii) response times of various organic compounds are in the range of 1 min or less; (iii) relatively high specificity; and (iv) relatively simple instrumentation. Membrane inlet mass spectrometry has found widespread use for the analysis of

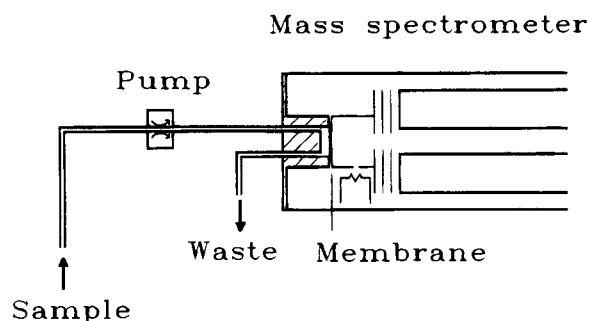


Figure 1. Schematic presentation of the membrane inlet mass spectrometric measurement system.

aqueous samples, biological and environmental in particular, whereas only a few examples of the analysis of contaminants dissolved in organic solvents (Degn and Bohátka, 1992; Lauritsen et al., 1992) have been published. In this study, membrane inlet mass spectrometry is for the first time applied for measurement of organic solvents in olive oil. It is shown that tetrachloroethylene and styrene can be measured at low parts per billion (ppb) levels directly from olive oil.

EXPERIMENTAL PROCEDURES

The membrane inlet mass spectrometric measurement system is shown in Figure 1. A clean olive oil stream was continuously supplied to the membrane inlet by a peristaltic pump (Watson-Marlow 101F, England) at a flow rate of 3.5 mL/min, and aliquots of olive oil samples were injected into this stream by manually transferring the inlet tube to the sample vessels. Typical injection time of the samples was 2 or 3 min, which means that the sample analysis can be done using less than 11 mL of olive oil. After each sample injection there is a waiting period of 3-4 min during which time clean olive oil is pumped through the inlet and the signal returns back to the base line level.

The membrane inlet was a flow-through type of inlet, which has been described in detail elsewhere (Lauritsen, 1990). It utilized a dimethyl silicone membrane (Technical Products Inc., Decatur, GA) with a thickness of 0.125 mm as the interface between the olive oil and the vacuum of the mass spectrometer. The temperature of the membrane inlet (45 °C) was controlled with a thermostated circulator water bath (Haake D1, Germany).

The mass spectrometer employed in these experiments was a Balzers QMG 420 mass spectrometer equipped with a gastight electron impact (70 eV) ion source. The mass

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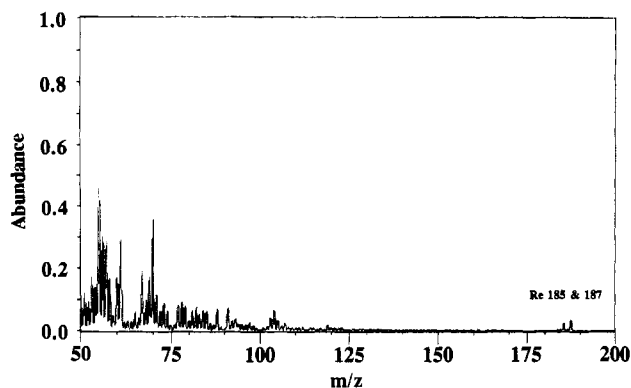


Figure 2. Electron impact ionization mass spectrum of olive oil (mass range 50–200). Note that the ions m/z 185 and 187 are rhenium ions from the filament.

spectrometer is a very simple and cheap residual gas analyzer type of mass spectrometer. Data were collected continuously either by measuring full mass spectra or by using the single ion monitoring method. The latter method was used to establish the detection limits and the linearity of response. Mass spectra of the low concentration solutions were recorded using background subtraction.

Several different commercial olive oils were used as samples. Stock solutions of olive oil containing styrene and/or tetrachloroethylene were prepared by directly adding commercial reagents (Fluka, Buchs, Switzerland) with a microliter syringe to a 1-L volumetric containing exactly 1 L of olive oil. The addition of solvents was done into the olive oil in order to minimize evaporation of these volatile solvents. After addition, the stock solution was vigorously mixed several times and allowed to equilibrate at least 30 min before serial dilutions with olive oil.

RESULTS AND DISCUSSION

A typical mass spectrum measured during continuous pumping of olive oil through the membrane inlet is presented in Figure 2. Mass spectra of three olive oil samples were measured during this study, but only small differences between the mass spectrum presented and the others were observed. The peaks in the measured olive oil mass spectra are believed to be due to aroma compounds in olive oil. An interpretation that is supported by the fact that the intensities of the ion peaks decreased about 5–10 times when a background mass spectrum of a oil sample, which was a mixture of soya oil, sunflower oil, and palm oil, was measured. The measured olive oil mass spectra showed also that the olive oil itself permeates the silicone membrane only to a very low degree and causes only slight interferences in styrene and tetrachloroethylene analysis. In fact, the pressure of the mass spectrometer decreased when olive oil was pumped through the membrane inlet compared to the situation in which water was pumped through the inlet.

In order to show identification capabilities of membrane inlet mass spectrometry, a spiked olive oil sample containing 250 ppb styrene and 90 ppb tetrachloroethylene was prepared. The background subtracted mass spectrum of this solution is presented in Figure 3. From the mass spectrum, styrene and tetrachloroethylene can be easily identified based on the characteristics ions, ions m/z 103 and 104 for styrene and ions m/z 129, 131, 133, 164, 166 and 168 for tetrachloroethylene. Note also that the theoretically expected isotopic ion ratios of tetrachloroethylene are well reproduced in the measured mass spectrum. The mass spectrum demonstrates that the sensitivity of the technique is good

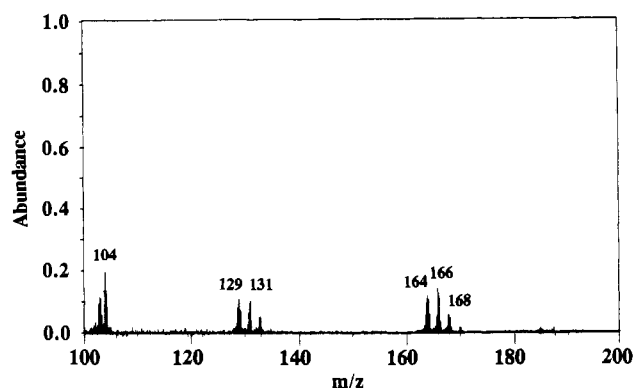


Figure 3. Background-subtracted electron impact ionization mass spectrum of olive oil sample spiked with 250 ppb styrene and 90 ppb tetrachloroethylene.

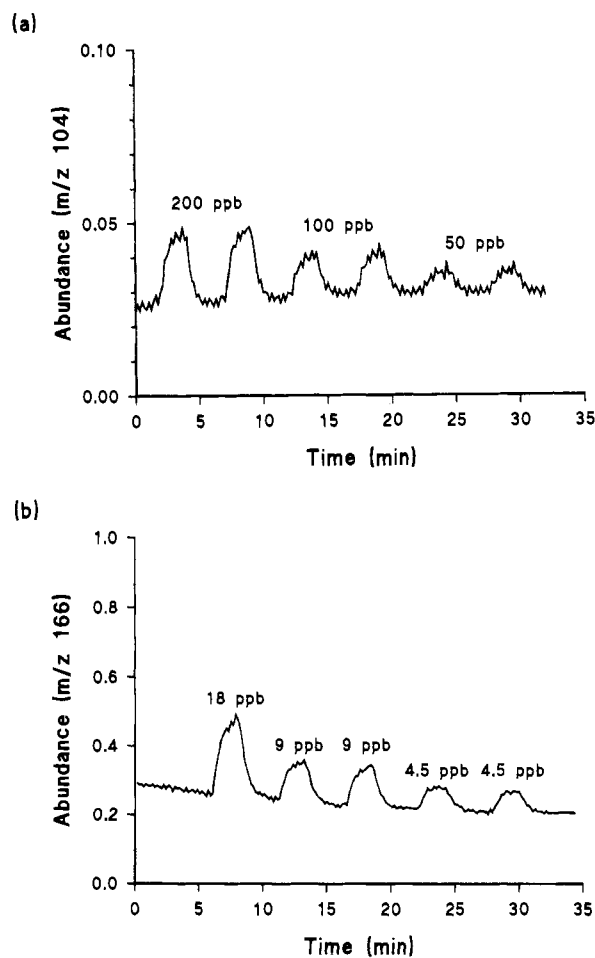


Figure 4. Single ion monitoring during successive injections of solutions of various concentrations in olive oil: (a) styrene, m/z 104 monitored, and (b) tetrachloroethylene, m/z 166 monitored.

enough for identification of impurities in olive oil at the ppb level.

Detection limits ($S/N = 3$) for styrene and tetrachloroethylene were measured operating the mass spectrometer in single ion monitoring mode. Single ion chromatograms for styrene (ion m/z 104) and for tetrachloroethylene (ion m/z 166) in the low parts per billion level is presented in Figure 4. Note that the concentration dependence and reproducibility of the signals are excellent. Detection limits of 100 ppb for styrene and of 5 ppb for tetrachloroethylene were found on the basis of several independent measurements. From Figure 4, it can be seen that rise and fall times

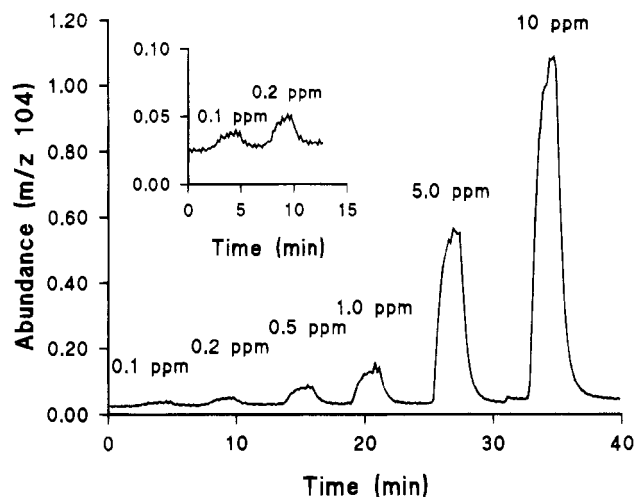


Figure 5. Single ion monitoring (m/z 104) during successive injections of solutions of increasing concentrations of styrene in olive oil.

(10–90%) of both analytes are in the order of 1 min. On the basis of Figure 4, it can also be calculated that 10–12 samples/h can be analyzed by this method. It is believed that the sample throughput can be even further enhanced by using automated flow injection analysis (FIA) methods for sample introduction, as has already been demonstrated in fermentation analysis by MIMS (Kotiaho et al., 1991; Lauritsen and Lloyd, 1994).

For quantitative purposes, good signal linearity as a function of analyte concentration is preferable. Linearity of MIMS for analysis of styrene and tetrachloroethylene in olive oil was tested using single ion monitoring mode and by sequentially injecting aliquots of spiked olive oil samples with increasing concentrations of styrene or tetrachloroethylene into the continuous olive oil stream going through the membrane inlet. As an example of the results, data measured for styrene in the concentration range of 0.1–10 ppm are shown in Figure 5. Already from Figure 5 it can be seen that the linearity of the response is excellent. This is also proven by the excellent correlations coefficient (r^2), 0.9999, calculated for the data presented in Figure 5. In a similar experiment for tetrachloroethylene, in the concentration range of 9 ppb–9 ppm, a correlation coefficient (r^2) of 0.9997 was obtained. Both of these data sets are presented in Figure 6 as a form of calibration curves. The results obtained show that in this MIMS application linear ranges at least 3 orders of magnitude can also be achieved, as has been demonstrated earlier in other applications of MIMS (Kotiaho et al., 1991).

In conclusion, good capabilities of membrane inlet mass spectrometry in direct measurement of styrene and tetrachloroethylene in olive oil have been demonstrated. More specifically, a detection limit of 5 ppb for tetrachloroethylene and a detection limit of 100 ppb for styrene were measured. It should be noted that the detection limit of tetrachloroethylene is clearly below the EU regulatory level, which is 100 ppb (Pocklington, 1992). The low detection limits obtained for styrene and tetrachloroethylene give a reason to believe that the method is also applicable for analysis of other volatile organic solvents. In addition, good signal linearity and fast response times were observed. The latter characteristic is important in the sense that it provides the basis for a large sample throughput and therefore the basis for the most sensible application of MIMS in olive

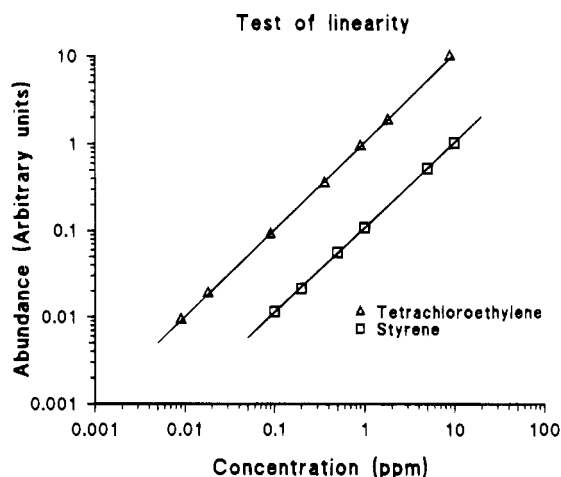


Figure 6. Styrene and tetrachloroethylene calibration curves in the ranges of 0.1–10 ppm and 9 ppb–9 ppm, respectively. Y-intercept for styrene line is 0.0039, and for tetrachloroethylene line it is -0.0432 .

oil analysis, i.e., screening of the presence of organic solvents in a large number of olive oil samples is possible and economical using membrane inlet mass spectrometry.

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