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## Supercritical fluid extraction for the determination of petroleum hydrocarbons in soil

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### Abstract

The supercritical fluid extraction (SFE) of petroleum hydrocarbons (PHCs) was carried out spiking a clay–sand soil with saturated and aromatic fractions from crude oil. The effect of acetone concentration in the supercritical fluid acting as a modifier was also investigated. The best recoveries of PHCs close to 70–100% were obtained at 80°C and 227 atm, corresponding to a fluid density of 0.65 g/ml of pure CO<sub>2</sub>, in the presence of 5% (v/v) acetone. The presence of the polar modifier (5%) improved the extraction of the aromatic fraction. Higher concentration of modifier (10%) decreased the extraction efficiencies of both saturated and aromatic fractions. The recovery of the aromatic compounds were proportional to the increase of analyte concentration in the spiking solutions. A combination of size-exclusion and adsorption effects seems to be involved and this would account for the higher recovery of low- and high-molecular-mass *n*-alkanes as compared to those of the mid ones. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

A number of quantitative applications of supercritical fluid extraction (SFE) for the extraction of pollutant from the soil have been reported [1].

In 1992 the US Environmental Protection Agency (EPA) approved the first SFE method in lieu of the conventional methods for the extraction of total petroleum hydrocarbons from contaminated soils which had been used until then [2]. Conventional methods including sonication and Soxhlet extraction are time-consuming and lead to the production of a large amount of waste solvents. With regards these

drawbacks, SFE has proven to be a valid alternative given the better mass transfer properties of supercritical fluids, shorter extraction times and ease of extract separation. The recovery of an analyte from a soil essentially depends on two factors, namely the solubility of the analyte in the supercritical fluid [3] and the mass transfer of the analyte from the soil matrix to the supercritical fluid [4]. Solubility is linked to the density and polarity of the supercritical fluid which may be controlled by the temperature and pressure in the extractor. The mass transfer of the analyte is related to both the nature of the analyte and soil structure and can be controlled by the mode of extraction, the type and density of the supercritical fluid used, extraction temperature and use of modifiers. Soils at sites involving industrial activities may be subject to pollution. For instance, petroleum

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hydrocarbons (PHCs) are a frequent source of contamination in the soil [5]. PHCs comprise extremely complex classes of compounds with a wide range of physical and chemical properties. The different solubilities and sorptions of the analytes in the supercritical fluid and on soil particles, respectively, make their extraction from the soil extremely problematic.

The present paper intends to discuss both the effects of the temperature and pressure on the selectivity of the supercritical fluid to extract the PHCs from the soil and the addition of an organic modifier such as acetone for enhancing the polarity of the supercritical CO<sub>2</sub> [6,7].

## 2. Experimental

### 2.1. Samples

A clay–sand test soil supplied by the Department of Agricultural Chemistry (University of Bologna) containing 3.16% of organic matter, 55.3% of sand, 14.6% of silt and 30.1% of clay (pH 7.40) was used.

### 2.2. Spiking solutions

The oil employed for the extraction of PHCs from soil was obtained by a preparative separation from a deasphaltenated crude oil purchased from AGIP Petroli (Rome, Italy). Deasphaltenation of heavy oil was performed by precipitating the asphaltenes with *n*-hexane in the crude oil with an organic solvent ratio of 1:30 (w/v) [8]. The saturated and aromatic fractions were separated from the deasphaltened crude oil by liquid–liquid extraction with dimethyl sulfoxide according to the procedure described by Natusch and Tomkins [9]. Saturated and aromatic fractions were dissolved in the minimum volume of *n*-hexane, thus representing the spiking solutions.

### 2.3. Spiking conditions

A weighed quantity of spiking solution was added to 7–8 g of soil in sealed bottles in order to obtain final concentrations equal to 0.02 g/g soil of saturated hydrocarbons (HCs) and 0.1 g/g soil of polycyclic aromatic hydrocarbons (PAHs). The sealed bottles were shaken for one day at 25°C to

make the spiking in the soil homogeneous and to equilibrate the sorption phenomena [10]. The spiked soil was dried at room temperature for 5 h in order to evaporate the excess of *n*-hexane. After this period, the samples were completely transferred into the extraction cells. All the experiments were performed three times under the same conditions.

### 2.4. Supercritical fluid extraction

A Hewlett-Packard Model 7650T instrument was employed for extraction. The sample of spiked soil was placed inside a 10-ml extraction cell. The modifier (acetone) in the required concentration, 5% or 10% (v/v), was added directly to the sample in the extraction cell. A 15 min static extraction period using CO<sub>2</sub>+modifier was followed by a 15 min dynamic extraction using CO<sub>2</sub> only. The flow-rate of supercritical CO<sub>2</sub> was 1 ml/min. The extraction conditions were 80°C and 227 atm corresponding to the fluid density of the supercritical CO<sub>2</sub> of 0.65 g/ml [11]. A solid trap (stationary phase: octadecylsilicate) was adopted as the collection system. The temperature trap was maintained at 30°C. Extracted analytes were collected into 1.5 ml of *n*-hexane. After each extraction, the solid trap was washed with 1.5 ml of acetone and 1.5 ml *n*-hexane which were checked for residual hydrocarbons.

### 2.5. Gas chromatographic analysis

PHC analyses were performed using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector using hydrogen as the flow. Injections were made in the splitless mode into a 25 m×0.25 mm I.D. (0.25 μm film thickness) methyl silicone column (Quadrex). The temperature of the injector and of the detector was maintained at 270°C. The oven temperature was kept at 40°C for 5 min, ramped to 90°C at 50°C/min, maintained for 1 min, ramped to 270°C at 4°C/min and maintained for 60 min. The concentration of the *i* identified hydrocarbon was proportional to the following ratio,  $C_i \propto fA_i/A_{st} C_{st} 1/M_r$  where  $A_i$  and  $A_{st}$  represent the area of the *i* hydrocarbon and of the internal standard (*n*-octane), respectively,  $M_r$  is the molecular mass of the *i* hydrocarbon,  $C_{st}$  is the internal standard concentration and  $f$  is the dilution factor.

### 3. Results and discussion

#### 3.1. Theoretical model

The sorption of the hydrocarbons on the organic matter in the soil is primarily induced by hydrophobic effects. The quantitative description of the relationship between the concentration of pollutants sorbed by the soil and the concentration in the solvent is given by a sorption isotherm. A general equation is the Freundlich isotherm,

$$S_{\text{eq}} = K_f C_{\text{eq}}^{1/n} \quad (1)$$

where  $S_{\text{eq}}$  is the concentration of pollutant sorbed by the soil at equilibrium,  $C_{\text{eq}}$  is the concentration of pollutant in solvent at equilibrium,  $K_f$  is the Freundlich sorption coefficient and  $n$  is an empirical constant.  $K_f$  depends on the specific adsorption and on the specific surface area of the sorbent.  $n$  is a power function related to the sorption mechanisms which are correlated to the mass transfer of the pollutant from the solvent phase to the active sites of the sorbent. The sorption process is a reaction in equilibrium with desorption so that Eq. (1) can also be used to describe analyte extraction from soil.

Recovery of the analyte from the soil,  $R_i$ , depends to a sum of flow equilibria due to the static and the dynamic extraction. However, for an infinitesimal range of extraction time, the recovery may be approximated to a static extraction following the equation,

$$R_i = C_{\text{eq}}/S_0 \quad (2)$$

where  $S_0$  is the total concentration of the analyte sorbed by the soil. The recovery of an analyte from the soil essentially depends on two factors, namely the solubility of the analyte in the supercritical fluid and the mass transfer of the analyte from the soil matrix to the supercritical fluid. Solubility is linked to the density and polarity of the supercritical fluid. The second factor affecting analyte recovery from soil depends on physico-chemical phenomena such as the diffusion of the solvent in soil porosity and the desorption of the analyte from the soil surface. Extraction time was optimized in our experiments so as to minimize the effect of the analyte diffusion within the soil structure.

Replacing the  $C_{\text{eq}}$  term of Eq. (1) in Eq. (2),

$$R_i = S_{\text{eq}}^n / K_f^n S_0 \quad (3)$$

as  $S_{\text{eq}} = S_0 - C_{\text{eq}}$ . Eq. (3) can be rewritten as

$$R_i = (S_0 - C_{\text{eq}})^n / K_f^n S_0 \quad (4)$$

The sorption isotherm of many non-polar organic analytes is linear when the value of  $n$  in Eq. (1) is equal to 1. On this basis, Eq. (4) becomes

$$R_i = (S_0 - C_{\text{eq}}) / K_f S_0 = (1 - R) / K_f \quad (5)$$

from which

$$R_i = 1 / (1 + K_f) \quad (6)$$

When  $n=1$ ,  $K_f$  is correlated to the free energy,  $\Delta G^0$ , for the mass transfer of the analyte from the solvent phase to the soil according to the following equation

$$K_f = \exp(-\Delta G^0 / RT) \quad (7)$$

and by including Eq. (7) in Eq. (6), the following equation is obtained:

$$R_i = 1 / [1 + \exp(-\Delta G^0 / RT)] \quad (8)$$

$\Delta G^0$  of the aliphatic and aromatic hydrocarbons usually decreases as the carbon number increases. Consequently,  $K_f$  increases while the capacity of the solvent to extract the analyte decreases.

The values for  $n$  of organic pollutants usually range from 1 to 5. Eq. (4) can be mathematically transformed in,

$$\begin{aligned} R_i &= (S_0 - C_{\text{eq}})^n / K_f^n S_0 \times S_0^n / S_0^n \\ &= (1 - R_i)^n S_0^{n-1} / K_f^n (1 - R_i)^n / R_i = K_f^n S_0^{1-n} \end{aligned} \quad (9)$$

Eq. (8) shows that as analyte concentration,  $S_0$ , increases the value of  $(1 - R_i)^n / R_i$  approaches 0 and consequently the recovery increases.

#### 3.2. Effect of the modifier

The presence of a polar modifier such as acetone in the supercritical fluid can improve the extraction of the aromatic compounds. The supercritical fluid

containing 5% (v/v) of acetone permitted one to recover 75% of the aromatic fraction from the spiked soil as compared to 60% when the modifier was not added. The acetone increased the polarity of the solvent causing a higher solubility of the aromatic compounds. No data are reported on the solubility of the hydrocarbon in this modified supercritical CO<sub>2</sub>. Vice versa, a high acetone concentration reduced aromatic fraction recovery as was observed when the supercritical fluid was used with an acetone content of 10%, in which case only 10% of the aromatic fraction was recovered. A similar behavior was already described by Reindl and Höfler [12]. Our experiments have further shown that the extraction yield of the saturated fraction was deeply decreased at the high concentration of modifier. A possible explanation for this behavior may be that the supercritical conditions of the modified CO<sub>2</sub> were not reached but little information is available in the literature on this point. However, acetone is a typical solvent which causes the paraffins in petroleum to precipitate, this means that the capacity to recover

the aliphatic compounds decreases as the modifier concentration is increased.

Acetone is often used as the solvent of the spiking solutions which contain aromatic compounds because it may exert a similar swelling action on the clay to that of water or alcohol [13]. Acetone in the supercritical fluid opens up the intracrystalline layers of the clay structure, thus allowing the supercritical CO<sub>2</sub> to interact with the trapped analytes. Acetone increases the solubility of the aromatic compounds in the solvent while also improving the interactions between the solvent and the little aromatic structures following on its swelling effect. For this reason the recovery of the saturated fraction is more homogeneous between the different *n*-alkanes but less efficient in the modified supercritical fluid. It may further be assumed that acetone competes with the analytes for the active sites on the matrix surface, thus favouring desorption processes. The concentration of acetone of 5% was chosen as an optimized condition in order to have the highest extraction efficiencies of the saturated and aromatic fractions.

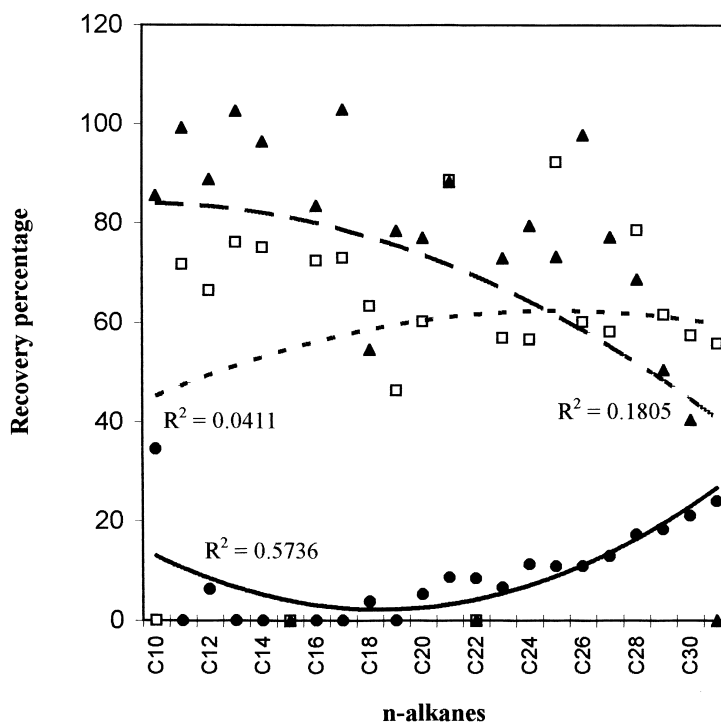


Fig. 1. Recovery percentage of the *n*-alkanes as a function of the carbon number at different concentrations of modifier, 0% (▲) (---), 5% (□) (···) and 10% (●) (—), in the supercritical fluid.

### 3.3. Recovery of the saturated fraction

In the absence of the modifier the recovery of the aliphatic compounds exhibits a parabolic trend with respect to the carbon number in which the mid-range-molecular-mass *n*-alkanes ( $C_{18}$ – $C_{35}$ ) are those most strongly retained in the soil. Thermodynamic and size-exclusion effects may account for the parabolic trend of the saturated fraction extraction in the absence of the modifier. The best extraction efficiencies of the low-molecular-mass *n*-alkanes

( $<C_{18}$ ) were ascribable to their weak force of sorption on the soil (Fig. 1). The high-molecular-mass *n*-alkanes ( $>C_{35}$ ) have a higher force of sorption on the soil but are poorly diffused through the matrix so that solvent and analyte interaction is favoured and the extraction capacity of the solvent therefore improves. In the presence of the modifier 5% (v/v), the low-molecular-mass *n*-alkanes showed worse extraction efficiencies as compared to those in the absence of modifier that is probably due to a decrease of the solubility in the supercritical fluid. In

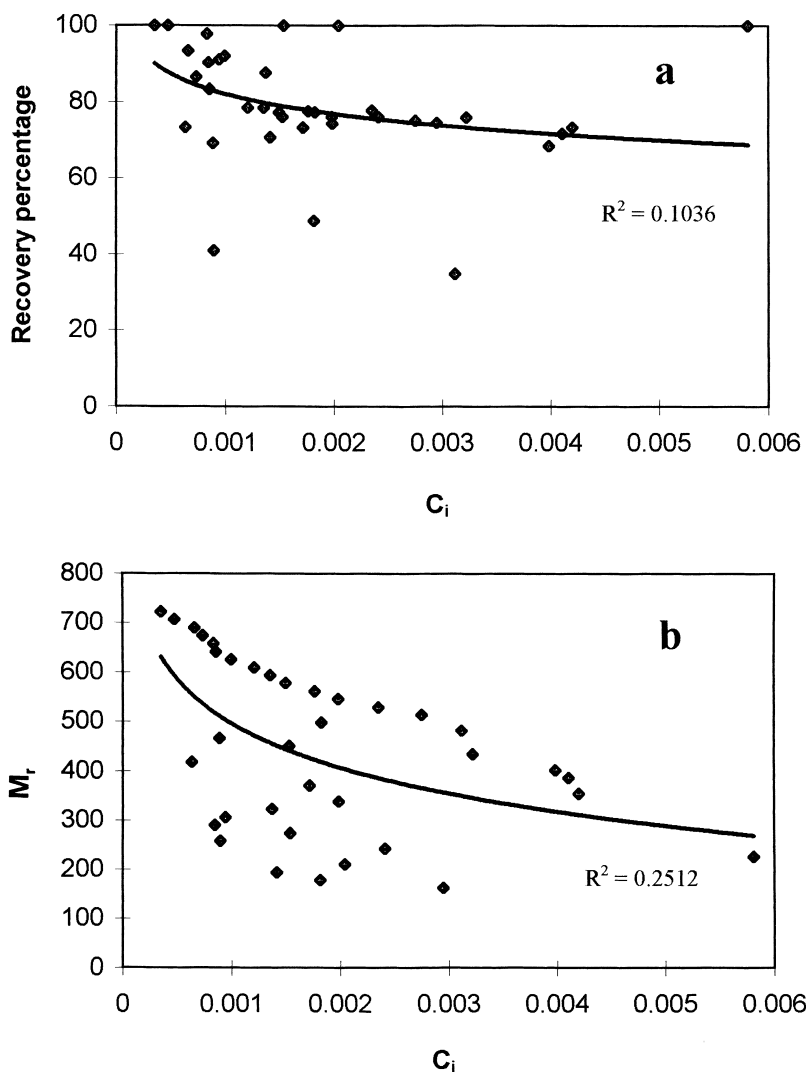


Fig. 2. Recovery percentage and molecular mass ( $M_r$ ) of the *n*-alkanes as a function of the concentration of each *i* compound,  $C_i$ , at 5% of modifier in the supercritical fluid.

contrast, the mid-*n*-alkanes exhibited a higher recovery that might be explained with a competitive effect of the acetone on the active sites of the matrix favouring in this way the desorption of the analyte. This double effect of the modifier on both the analyte solubility in the supercritical fluid and the competition on the active sites of the matrix was confirmed by the opposite behavior of the recoveries in the presence of 10% (v/v) modifier. The decrease of the solubility of the *n*-alkanes in the supercritical fluid resulted in a general lower extraction efficiencies. In particular, the recoveries increased as the molecular mass of the *n*-alkanes increased. This means that the competitive effect of the acetone prevails over the solubility effect of the modified supercritical fluid.

The comparison of the results in Fig. 2a and b showed that, in the presence of the modifier (5%, v/v), the recovery of the saturated fraction increased as molecular mass increased and slightly decreased as analyte concentration increased. The controversial behavior with respect to the model of Eq. (8) is probably due to the effect of the modifier on the solubility of the low-molecular-mass *n*-alkanes in the supercritical fluid.

### 3.4. Recovery of the aromatic fraction

In the absence of the modifier, the recovery of the high-molecular-mass PAHs (>trimethylnaphthalenes) are higher than those of their low-molecular-mass homologues as they are poorly diffused through the matrix (Fig. 3). In the presence of 5% (v/v) acetone, the improved recovery of the low-molecular-mass compounds is probably due to the swelling effect of the modifier. The extraction efficiencies of the aromatic compounds increased as analyte concentration increased (Fig. 4) as described by Eq. (8) while the effect of molecular mass appeared to be negligible (Fig. 3).

The dependence of recovery on analyte concentration suggests that extraction efficiency is controlled by thermodynamic factors. In fact the recovery is linked to the equilibrium between the process of sorption and desorption of the analyte on the soil [Eq. (1)] as well as to the partition coefficient between the analyte and the supercritical solvent [14].

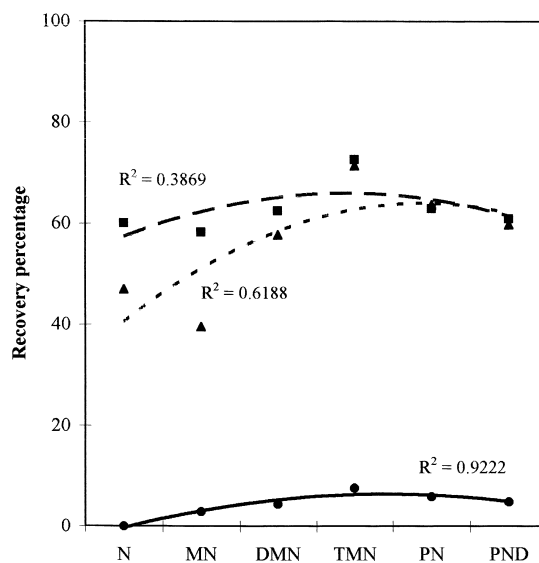


Fig. 3. Recovery percentage of some identified aromatic compounds at different concentrations of modifier, 0% (▲) (---), 5% (◻) (···) and 10% (●) (—), in the supercritical fluid (N = naphthalenes, MN = methylnaphthalenes, DMN = dimethylnaphthalenes, TMN = trimethylnaphthalenes, PN = phenanthrene, PND = phenanthrene derivatives).

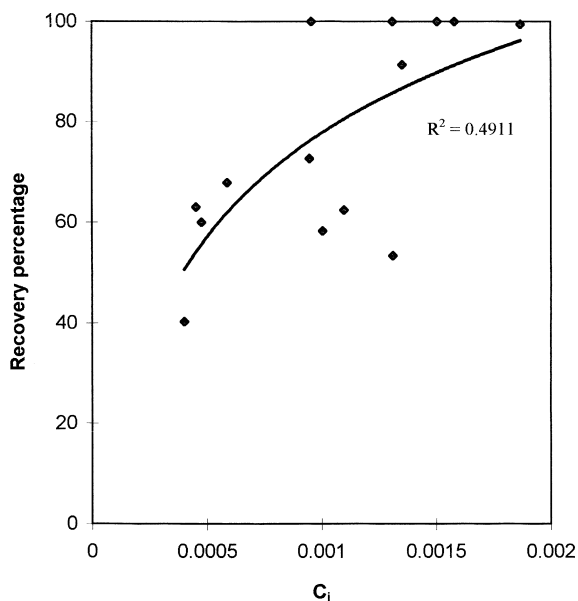


Fig. 4. Recovery percentage of the identified aromatic compounds as a function of the concentration of each *i* compound,  $C_i$ , at 5% of modifier in the supercritical fluid.

#### 4. Conclusions

For the successfully performed SFE of hydrocarbons from contaminated soils, the extraction parameters must be carefully chosen. Matrix and analyte properties play a very important role in the choice of the extraction conditions. Our findings have shown that the addition of an organic modifier such as acetone to the supercritical fluid changes the selectivity for the extraction of the different components making up the saturated and aromatic fractions of a crude oil. The results suggest that acetone can modify the solvent properties of the supercritical fluid while also exerting a swelling action on the matrix, thus favouring the desorption process of the analyte.

The study of simplified model systems, such as spiked samples, can be useful to understand the limiting factors for the development of a standardized methodology for quantitative SFE. It may be of interest for determining the amount of hydrocarbons present in contaminated soil as well as the fate of the pollutants during the remediation and/or bioremediation processes.

#### References

- [1] G.K.C. Low, G.J. Duffy, *Trends Anal. Chem.* 14 (1995) 218.
- [2] B. Lesnick (US Environmental Protection Agency, Office of Solid Waste), announcement at the EPA SFE Workgroup meeting, Washington, DC, 17 July 1992.
- [3] G.S. Gurdial, N.R. Foster, *Ind. Eng. Chem. Res.* 30 (1991) 575.
- [4] J. Pawliszyn, *J. Chromatogr. Sci.* 30 (1993) 403.
- [5] R. Bartha, *Microb. Ecol.* 12 (1986) 155.
- [6] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawliszyn, *Anal. Chem.* 66 (1994) 909.
- [7] J. Hollender, J. Shneine, J. Dott, W. Heinzel, M. Hagemann, H.W. Gotzke, *J. Chromatogr. A* 776 (1997) 233.
- [8] L. Setti, G. Lanzarini, P.G. Pifferi, G. Spagna, *Chemosphere* 26 (1993) 1151.
- [9] M. Natusch, B.A. Tomkins, *Anal. Chem.* 50 (1978) 1429.
- [10] L. Morselli, L. Setti, A. Iannuccilli, G. Spinuzzi, G. Dinnelli, G. Quattroni, *Ann. Chim. (Rome)* 88 (1998) 545.
- [11] S. Eckert-Tilotta, S.B. Hawthorne, D.J. Miller, *Fuel* 72 (1993) 1015.
- [12] S. Reindl, F. Höfler, *Anal. Chem.* 68 (1994) 1808.
- [13] T.M. Fahmy, M.E. Paulaitis, D.M. Johnson, M.E.P. McNally, *Anal. Chem.* 65 (1993) 1462.
- [14] G.A. Montero, K.B. Schnelle, T.D. Giorgio, *J. Environ. Sci. Health* 32A (1997) 481.