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Simultaneous determination of methyl *tert*-butyl ether, its degradation products and other gasoline additives in soil samples by closed-system purge-and-trap gas chromatography–mass spectrometry

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Abstract

A new protocol for the simultaneous determination of methyl *tert*-butyl ether (MTBE); its main degradation products: *tert*-butyl alcohol (TBA) and *tert*-butyl formate (TBF); other gasoline additives, oxygenate dialkyl ethers: ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and diisopropyl ether (DIPE); aromatics: benzene, toluene, ethylbenzene and xylenes (BTEX) and other compounds causing odour events such as dicyclopentadiene (DCPD) and trichloroethylene (TCE) in soils has been developed. On the basis of US Environmental Protection Agency (EPA) method 5035A, a fully automated closed-system purge-and-trap coupled to gas chromatography/mass spectrometry (P&T-GC/MS) was optimised and permitted to detect μg/kg concentrations in solid matrices avoiding losses of volatile compounds during operation processes.

Parameters optimised were the sampling procedure, sample preservation and storage, purging temperature, matrix effects and quantification mode. Using 5 g of sample, detection limits were between 0.02 and 1.63 μg/kg and acceptable method precision and accuracy was obtained provided quantification was performed using adequate internal standards.

Soil samples should be analysed as soon as possible after collection, stored under −15 °C for not longer than 7 days if degradation products have to be analysed. The non-preservative alternative (empty vial) provided good recoveries of the most analytes when freezing the samples up to 7 day holding time, however, if biologically active soil are analysed the preservation with trisodium phosphate dodecahydrate ($Na_3PO_4\cdot 12H_2O$ or TSP) is strongly recommended more than sodium bisulphate ($NaHSO_4$). The method was finally applied to provide threshold and background levels of several gasoline additives in a point source and in sites not influenced by gasoline spills. The proposed method provides the directions for the future application on real samples in current monitoring programs at gasoline pollution risk sites where till now little monitoring data for MTBE in soils are available.

Keywords: MTBE; BTEX; Fuel oxygenates; Closed-system purge-and-trap; GC–MS; Soil

1. Introduction

Volatile organic compounds (VOCs) are among the most frequently identified contaminants in soil and groundwater samples during the investigation of suspected hazardous waste sites. Because some VOCs and their degradation products are potentially mutagenic, carcinogenic or teratogenic, their concentrations in both matrices are key factors in the risk assessment process [1].

In particular, environmental contamination with VOCs associated with fuel/petroleum usage is widespread in the world. Fuel oxygenates are added to gasoline since the 1970s mainly as octane enhancers that increase combustion efficiency and reduce toxic air emissions such as lead compounds or carbon monoxide. MTBE became the most commonly used oxygenate and one of organic chemical with the highest production volume worldwide [2]. In Europe, large amounts of MTBE ($2–3 \times 10^9$ kg) are produced each year and its content in gasoline can comprise up to 12–14% (v/v) [3,4]. As a result of its intense use, MTBE has become one of the most frequently detected volatile organic compounds in groundwater and can be adsorbed on subsurface solids [5]. However, MTBE's relatively low partitioning coefficient to organic carbon ($K_{oc} = 41$ versus $K_{oc} = 191$ for benzene [6]) indicates that it will preferentially remain in the water phase instead of adsorbing onto soil organic matter [7]. For example, Squillace et al. [5] calculated that in a sand aquifer with moder-

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ate organic carbon content (0.1%), only 8% of the total mass of MTBE was sorbed to the organic matter whereas 92% remained in solution. By contrast, 39% of the total mass of benzene and 72% of ethylbenzene were sorbed to the organic matter. Similar to MTBE, sorption of *tert*-butyl alcohol (TBA) and *tert*-butyl formate (TBF) to soils will be minimal, so infiltration and migration of these degradation products will be essentially accelerated in the subsurface [8].

Accidental spills during transport and leaking underground storage tanks (LUST) in petrol stations or refineries are responsible for the highest MTBE pollution events. In recent years, high concentrations of this fuel oxygenate have been reported in some groundwater tables not only of USA (for example, up to 46 mg/L in Delaware [9]) but also of Europe (from 120 μg/L to 830 mg/L [3,10–12]) and represent a great soil contamination risk. To date, maximum permissible levels of MTBE in any environmental compartment have not yet been established in Europe. However, MTBE soil action and cleanup levels (both from 5 μg/kg) set up in USA can be used as reference in the analysis of MTBE in soils at LUST sites [13]. Furthermore, little monitoring data for MTBE in soils in Europe are available so far [4].

In general, the determination of VOCs in soil and sediment samples at low μg/kg level aims at the development of validated sensitive methods that permit unequivocal identification of target compounds. Among others, purge-and-trap (P&T) and headspace (HS) coupled with mass spectrometry (MS) are the most commonly used and offer the best results according to the stated quality assurance/quality control requirements [14].

Recently, other sample concentration and preparation alternatives such as headspace solid-phase microextraction (HS-SPME) have been applied successfully to the analysis of chlorinated hydrocarbons [15] or benzene, toluene, ethylbenzene and xylenes (BTEX) [16,17]. Also pressurized liquid extraction (PLE; Dionex trade name ASE for accelerated solvent extraction) has been shown to be used for higher concentrations (mg/kg) of BTEX in soils by a mixture of hexane/acetone (1:1) [18]. A semiautomatic purge-and-membrane inlet mass spectrometric (PAM-MS) instrument [19] provided limits of detection ranging from 5 to 50 μg/kg for some BTEX compounds or from 40 to 100 μg/kg for ether oxygenates (MTBE, TAME) depending on soil type [20].

Among different types of P&T instruments assembled for analysis of VOCs in solid matrices [21–27], closed-system P&T are directed to determine low-concentration (<200 μg/kg) VOCs in soil samples, as indicated in EPA Method 5035 [28]. This system was used to analyse relatively new volatile pollutants such as the fuel oxygenates in soil [29]. The major advantages of closed-system technique are (i) the minimization of volatile losses using a hermetically-sealed sample vial that is never broken or exposed to the atmosphere after sampling; (ii) the use of water which improves VOCs desorption and eliminates differences between types of soils [15,16,20,30] rather than dry soil purge or methanol extraction and (iii) heating control. The combination of closed-system P&T-GC/MS can provide the best sensitivity, easy automation, non-requirement for pre-treatment of samples and non-production of flammable waste.

An important issue when analysing fuel oxygenates in soil is sample collection and preservation. Soil samples collected by different sampling methods yielded markedly different soil VOC concentrations [31]. In a first step, experiments were performed on homogeneous samples that exclude the systematic error associated with sample collection and handling [32]. Nowadays, special single-use cores are commercially available and they are designed to eliminate the need for a field portable balance, separate handle or cutting off syringes. The principal purpose of their use is to reduce the amount of disturbance when collecting solid samples for the analysis of VOCs. The EnCore samplers (En Novative Technologies, Green Bay, WI, USA) can be additionally capped to make a gas-tight container, a short-time holding vessel until analysis. But these samplers, recommended by the EPA method and some other studies [33,34] may be economically unfeasible for some users. A cheaper alternative from the same company (En Novative Technologies) is Terra Core sampler, one-time use plastic transfer tool, designed to easily take 5 g samples and transfer to appropriate containers in the field.

Soil samples should be properly preserved to avoid losses of MTBE, their degradation products or other fuel oxygenates, for instance, the addition of 1 g of sodium hydrogensulphate ($NaHSO_4$) combined with low storage temperatures increases the sample holding time from 48 h to 2 weeks. The premise for reducing the temperature is that VOCs are volatile at room temperature, but their volatility decreases as the temperature falls off. The most common method of preservation is to cool the sample to 4 °C because it represents the temperature at which pure water exhibits its maximum density, hence its minimum volume. But for biologically active soils, this is not enough where freezing or using chemical preservatives that act as biocides are required. EPA method advised that care should be taken when freezing to prevent possible container breakage and never below −20 °C because of potential problems with vial seals and the loss of constituents upon sample thawing [29]. However, Alvarado and Rose [35] pointed out the use of subzero refrigerator system at −80 °C for the analysis of carbon tetrachloride in soil and vegetation samples as the key point of their protocol. On the other hand, another common technique such as field sample preservation with methanol is not appropriate for the analysis of low concentrations of VOCs by the closed-system P&T equipment.

In the light of this state-of-the-art, the objectives of the present study were focussed on the trace determination of MTBE, its main degradation products, TBA and TBF; other gasoline additives, oxygenate dialkyl ethers: ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and diisopropyl ether (DIPE); aromatics or BTEX compounds and other pollutants causing odour events such as dicyclopentadiene (DCPD) and trichloroethylene (TCE) in soils by a fully automated closed-system P&T-GC/MS using the novel SOLATek 72 Multi-Matrix Vial Autosampler purchased by Tekmar–Dohrmann, USA. The analytical protocol reported in this study comprises (i) to optimize the best purge-and-trap conditions, (ii) to perform quality control and quality assurance studies and (iii) to optimize the preservation and storage procedures. The performance of the method was assessed by analysing spiked and environmental soil and sediment samples containing varying concentration of