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Vigilància ambiental de metil *tert*-butil èter (MTBE), un additiu de la gasolina, en aigües i sòls

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3 METODOLOGIA I APLICACIÓ DE P&T-GC/MS PER A L'ANÀLISI DE SÒLS

3.1 INTRODUCCIÓ

3.1.1 Els sòls

El resultat final del procés de meteorització d'una roca és la formació d'un sòl, és a dir, d'una capa superficial de materials lliures i gruix variable, on hi ha espais interparticulars on poden coexistir aire i aigua. El sòl, no és solament mineral, és un sistema dinàmic sota la influència dels agents atmosfèrics i els éssers vius que en depenen. Les substàncies orgàniques, en vies de mineralització, es combinen amb altres elements (orgànics o inorgànics), donant lloc a estructures complexes que confereixen noves i interessants propietats al sòl.

Per tal de classificar de forma bàsica un sòl objecte d'estudi (no específicament com ho faria l'edafologia), es solen indicar els següents paràmetres:

- Fondària a la qual s'ha pres la mostra de sòl. Superficials (pocs cm) o profunds (m).
- Composició en matèria orgànica i inorgànica. Un dels indicadors més emprats és l'anàlisi del carboni orgànic total (TOC).
- Humitat del sòl (%), per la diferència de pes entre el sòl original i un cop assecat a 105ºC durant tota la nit o bé liofilitzat.
- Textura o classificació del material mineral per la seva grandària (graves, sorres, argiles, llims o fangs).

Totes aquestes característiques del sòl, així com les propietats físico-químiques dels compostos estudi (constants de partició) o bé certa informació sobre la possible font de contaminació (difusa-puntual, des de la superfície o bé en profunditat, etc.) ja ens donaran una idea sobre com s'estaran distribuint els compostos als diferents compartiments ambientals de la zona d'estudi.

3.1.2 Tècniques generals d’extracció de VOCs en sòls

En general, la determinació de VOCs en sòls i sediments a nivells baixos (μg/kg) requereix mètodes sensibles que permetin la identificació inequívoca dels compostos d’estudi. Els protocols estandarditzats per l’anàlisi de contaminants en matrius sòlides es recullen en una sèrie de mètodes EPA que es van renovant al llarg dels anys, com ara el mètode de caire general per l’anàlisi de residus sòlids, EPA SW-846, de l’any 1986 [136] i renovat al 1996 [137] i del qual se’n deriven diferents tècniques d’extracció: 5030/5035 (P&T), 5031 (destil·lació azeotròpica i DAI), 5032 (destil·lació per buit) i 5021 (HS); acoblades a altres de separació i detecció. En el cas dels VOCs, es descriuen tècniques basades en GC acoblada a FID (8015), PID (8021) i MS (8260).

Com en el cas de les aigües, la utilització de tècniques d’extracció per VOCs (usualment P&T i HS) acoblades a un MS han estat les que tradicionalment han ofert els millors resultats d’acord amb els paràmetres de qualitat de la USEPA [137]. Tot i que recentment, s’han desenvolupat amb èxit altres tècniques com el HS-SPME aplicat a l’anàlisi de hidrocarburs clorats [138] i BTEX [123,139,140]; així com un innovador sistema semiautomàtic de purga i membrana (PAM) connectat a un MS [141,142].

3.1.3 P&T aplicat a mostres sòlides, avenços tecnològics

Des que la tècnica de P&T va ser desenvolupada per a l’anàlisi d’aigües al 1974 [125], els esforços per adaptar-la a l’anàlisi de mostres sòlides s’han anat succeint amb un gran nombre de millores tecnològiques. L’any 1991, Bellar [88] aconseguia modificar el P&T per a l’anàlisi de VOCs en sòls, però aquesta tècnica encara patia de ser un procediment principalment manual i no podia competir enfront les tècniques automatitzades o fàcilment transportables al camp com ho era llavors el HS [143,144]. Va ser aleshores quan Bianchi et al. [145,146] va desenvolupar una modificació de l’aparell immers en un bany calent i agitat a intervals regulars connectat amb una unitat de desorció tèrmica automàtica (ATD-50). Aquest instrument requeria grans quantitats de mostra (300-400 g), llarg períodes de purga (70 min) i elevats cabals d’heli (100 mL/min); però suggeria que les recuperacions d’alguns VOCs podien millorar-se a elevades temperatures (60ºC). Aquest mètode aconseguia bons límits de detecció (0.01-

0.1 μg/Kg) per la majoria dels VOCs d'estudi i es va fer servir per detectar per primer cop MTBE en sediments marins [145], però no se'n oferien detalls dels resultats.

Més tard, es desenvolupaven instruments que permetien l'anàlisi de quantitats menors de mostra (pocs grams), però l'extracció dels VOCs encara es realitzava en sistemes oberts (mètode EPA 5030) i, en la majoria dels casos, es feia servir una extracció prèvia amb metanol en un bany d'ultrasons [147-149]. Els principals inconvenients eren, doncs, la pèrdua de sensibilitat per la subseqüent dilució de la solució metanòlica en aigua i les pèrdues dels compostos volàtils al llarg de la manipulació [144]. Tot i que, un cop en metanol, els VOCs podien ser emmagatzemats per llargs períodes de temps a -20 ºC sense una alteració significativa dels resultats (recuperacions del 89% al cap de 50 dies) [147].

Els avenços tecnològics, permetien al 1996, la promulgació del mètode EPA 5035 [150] on l'anàlisi de baixes concentracions de VOCs en sòls (<200 μg/kg) es feia possible gràcies a un procés completament tancat. Tanmateix, per concentracions superiors, es recomanava la dilució en metanol i aigua com es feia al mètode obert tradicional. Posteriorment, al juliol de 2002, una revisió d'aquest mètode (5035A) [89] es publicava amb l'ampliació de la llista de VOCs d'estudi (incorporant els additius oxigenats) i indicava algunes recomanacions de caire general per al seu anàlisi.

Els principals avantatges i inconvenients d'aquesta tècnica es troben recollits a la *Taula 13*.

Taula 13.-Principals avantatges i inconvenients del sistema de P&T tancat per a l’anàlisi de VOCs en sòls

Avantatges	***Inconvenients***
☺ No requereix pretractament.	☹ Preu de l’equip elevat
☺ Mínimització de la manipulació de la mostra.	☹ Risc de contaminació del sistema quan s’analitzen mostres molt concentrades.
☺ Mínimització de les pèrdues volàtils, durant el transport i l’anàlisi gràcies a la utilització de vials tancats hermèticament, que no tornen a ser oberts o exposats a l’atmosfera, un cop presa la mostra.	☹ Mostres més elevades de 200 µg/kg requereixen dilució en metanol i posteriorment en aigua.
☺ Límits de detecció situats al voltant dels 0,2 µg/kg.	☹ Possibilitat de degradació dels compostos tèrmicament inestables.
☺ En principi, no requereix de la utilització de dissolvents tòxics o inflamables.	☹ Les mostres només poden ser analitzades un cop.
☺ Totalment automatitzat.	☹ Curts períodes d’emmagatzematge de les mostres.
☺ La utilització d’aigua com a extractant, millora les recuperacions dels VOCs respecte tècniques de purga o equilibri (HS) en sec. I elimina les diferències entre sòls amb diferent % d’humitat.	☹ A Espanya, encara en fase d’experimentació (pilot). Els problemes tècnics no totalment resolts.
☺ Fa possible el control de la temperatura de purga en un ampli ventall (25-100 ºC)	

3.1.4 El problema del MTBE en sòls

Com en el cas de les aigües, no existeixen actualment nivells màxims establerts a Europa relatius a la contaminació de sòls per MTBE. A EEUU tampoc existeixen mesures de remeiació a nivell estatal, per això la regulació és força irregular. Per exemple, a l’any 2000, 34 dels 50 estats requerien de la vigilància ambiental (presa de mostres i anàlisi) de MTBE als sòls afectats per fonts puntuals de contaminació, concretament tancs d’emmagatzematge subterranis amb pèrdues de gasolina (LUST) [151]. En aquests estats, els nivells a partir dels quals s’havia d’emprendre accions paliadores o neteja completa de les zones contaminades eren enormement divergents (des de 5 µg/kg fins 319 g/kg), amb una mitjana de 300 µg/kg.

Si el que es pretén es protegir les aigües subterrànies dels efectes desagradables de gust i olor del MTBE, s'haurien d'establir estàndards més baixos, com indicava l'estudi de Rong i Wang [152]. Emprant el model de simulació de Monte Carlo pel càlcul de risc d'excedir els criteris de qualitat de l'aigua per MTBE, els autors van concloure que establint un llindar màxim de contaminació de 5 µg/kg hi hauria un 95% de probabilitat, mentre que amb 10 µg/kg es reduiria a un 50%, de que l'aigua subterrània no excedís l'objectiu de qualitat de 13 µg/L [152].

A Europa, existeix poca informació sobre els nivells de MTBE al sòl, tant afectats per fonts de contaminació difusa (soroll de fons) com puntual [153]. De fet, com en el cas de les aigües, parlar de concentracions típiques de MTBE en sòls seria difícil degut al diferent ús que se'n fa a diferents països i al ampli ventall de concentracions trobades a les aigües subterrànies (de ng/L a mg/L) i que podrien influenciar la seva adsorció en els materials de l'aqüífer.

En general, l'adsorció de MTBE als sòls hauria de ser baixa, doncs degut a les seves propietats físico-químiques, només un 8% del total del compost s'adsorbiria en els materials de l'aqüífer, usualment pobres en matèria orgànica (0,1%) [33]. Tot i això, l'estudi del risc ambiental del MTBE realitzat a Europa [154] mostra un ampli interval de concentracions als llocs afectats per fonts puntuals a Finlàndia, amb nivells per sota dels límits de detecció (<20 µg/kg) fins els 100 mg/kg, i un cas extrem a 1 g/kg.

Amb tot, la falta de mètodes estandaritzats per a l'extracció de MTBE dels sòls o de la fase gas d'aquests, evidencia encara més la necessitat de desenvolupament de metodologies pràctiques per a la determinació del compost que permetin un coneixement més ampli de l'impacte real del contaminant al medi ambient [155].

3.1.5 Material i instrumentació addicionals

Com s'ha esmentat al capítol 2, al gener de 2003 es procedia a la instal·lació d'un nou injector automàtic anomenat *SOLATek 72 Multi-Matrix Vial Autosampler* (*Figura 20*) que permetia l'anàlisi tant d'aigües com de sòls, aquests últims en acompliment del mètode EPA 5035 o sistema tancat.

Figura 20.-Nou injector SOLATek 72 Multi-Matrix Vial per a l'anàlisi de VOCs en aigües i sòls.

A més d'algunes millores tècniques generals, ja esmentades, combina la neteja a elevada temperatura, 90ºC, amb múltiples escombratges de neteja pressuritzats i tubs i agulles de baixa adsorció de VOCs com el Teflon o el Silcosteel®. Bàsicament, aquest instrument permet l'anàlisi de seqüències automàtiques de sòls i sediments dins del propi vial (no com les aigües que es purguen en un recipient de vidre independent al concentrador), incorporant aigua de cromatografia i una solució de PIs a través del sèptum, un corrent d'heli en la part inferior de l'agulla i la recollida dels VOCs arrossegats des de la barreja (sòl-aigua) per la part superior de la mateixa. Mentrestant la mostra es escalfada i agitada magnèticament. Per aquest últim requisit, es van haver de comprar agitadors magnètics amb forma de creu.

3.2 OPTIMITZACIÓ I APLICACIÓ DEL MÈTODE

A continuació l'**article 5** "*Simultaneous determination of methyl tertiary butyl ether, its degradation products and other gasoline additives in soil samples by closed-system purge-and-trap-gas chromatography–mass spectrometry*" ofereix una detallada i raonada descripció del procés d'optimització i desenvolupament del sistema tancat de P&T-GC/MS per a l'anàlisi dels additius oxigenats, aromàtics, productes de degradació principals del MTBE i ETBE, i altres VOCs d'interès com el TCE i el DCPD en sòls i sediments. El mètode agafa com a punt de partida els paràmetres i les recomanacions generals del mètode EPA 5035A, per tal d'adaptar-les o comprovar-ne la seva eficàcia amb els nostres compostos d'estudi. A més de l'optimització relativa als paràmetres lligats a l'anàlisi (com ara la temperatura de purga o la preparació de patrons o mostres fortificades), el control de qualitat (LODs, precisió, etc.), o bé la quantificació dels analits (efectes matriu, rectes de calibratge, ús de PIs, etc.); també es discuteix en profunditat un protocol per a la correcta presa de mostres (mostrejadors disponibles al mercat), les mesures de precaució relatives a la conservació (temperatura i temps d'emmagatzematge previ a l'anàlisi) i preservació (utilització d'additius químics que modifiquen el pH) de les mostres sòlides d'estudi (sòls i sediments). Tots els resultats obtinguts es correlacionen amb les propietats físico-químiques de cadascun dels compostos d'estudi.

A més, es mostren els primers resultats de l'aplicació del mètode en mostres de sòls reals afectats o no per fonts de contaminació per gasolina, en superfície i en profunditat (>0.5 m). Els valors obtinguts es comparen amb un dels pocs articles que presenta valors de MTBE i BTEX en sòls superficials i profunds a Europa [156].

Article científic (Art. 5):

“Simultaneous determination of methyl tertiary 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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Simultaneous determination of methyl tertiary 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 tertiary (*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 odor events such as dicyclopentadiene (DCPD) and trichloroethylene (TCE) in soils has been developed. Based on 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 optimized 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 to 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 ºC for not longer than 7 days if degradation products have to be analyzed. 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 active biologically 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 up to now little monitoring data for MTBE in soils are available.

Keywords: MTBE, BTEX, fuel oxygenates, closed-system purge-and-trap, GC-MS, soil.

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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 which 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 Mt) are produced each year and its content in gasoline can comprise up to 12-14% volume [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 (Koc= 41 v. Koc= 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 moderate 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 the responsible of the highest MTBE pollution events. In recent years, high concentrations of this fuel oxygenate have been reported in some groundwater tables 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 spectrometer (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 micro extraction (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 the 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 which is never broken or exposed to the atmosphere after sampling; (ii) the use of water which improve VOCs desorption and eliminate 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 analyzing 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 additionally be 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 gram-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 bisulphate ($NaHSO_4$) combined with low storage temperatures increases the sample holding time from 48 hours 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 ºC 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 is required. EPA method advised that care should be taken when freezing to prevent possible container breakage and never below -20 ºC due to 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 ºC 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 analyzing spiked and environmental soil and sediment samples containing varying concentration of target compounds in order to provide a robust, fully automated and reliable methodology for the analysis of gasoline additives in solid samples.

2. Experimental

2.1. Chemicals and materials

Standards were prepared from methanolic solutions at 2,000 mg/L (TAME and HC-BTEX/MTBE Mix) and 5,000 mg/L (TCE) or single compound neat stock solutions (ETBE, DIPE, TBA, DCPD) purchased from Supelco (Bellefonte, PA, USA) and TBF from Aldrich, (Steinheim, Germany). Fluorobenzene and 1,2-dichlorobenzene-d4 (EPA 524 Internal Standard Mix from Supelco) were used as internal standards (IS). Each compound was obtained in the highest purity that was commercially available (98.3 – 99.7%) and used as received within 4 weeks. Working standard solutions (studied compounds and IS) were prepared separately in ultra pure methanol and added on organic-free water (Merck, Darmstadt, Germany).

Different solid matrices were used for the optimization experiments (i) raw Ebro river basin sediments (Spain) composed by 33% sand (fraction >500 µm, 0.06% total organic carbon (TOC)), 44% clay (fraction between 120-500 µm, 0.31% TOC) and 22% silt (fraction <120 µm, 0.7% TOC) and 21% water content and (ii) the freeze-dried and homogenized urban soil from around 4 meters underground containing 63% stones and sand (fraction >500 µm), 20% clay (fraction between 120-500 µm, 0.15% TOC), 17% silt (fraction <120 µm, <0.1% TOC) and 8% water content. However, to have a homogeneous sample, the biggest particles were removed and the <500 µm fraction was used.

For preservation experiment, sodium hydrogen sulphate monohydrate ($HNaO_4S{\cdot}H_2O$) and tri-sodium phosphate *tert*-dodecahydrate ($Na_3O_4P{\cdot}12H_2O$) were purchased by Fluka (Sigma-Aldrich, Buchs, Switzerland).

2.2. *Sample collection*

Soil samples were collected in contaminated and non-contaminated sites to evaluate the performance of the sampling procedure, to demonstrate the applicability of the method and finally to determine threshold, background levels in sites known not to be influenced by point source and levels in contaminated sites. Samples were collected with a Terra Core sampler (En Novative Technologies) from the surface (gasoline station, high traffic area and abandoned gas work station) or at > 0.5 m depth (gas work station). Prior to surface sampling, the upper layer was swept. For deep soil sampling, the soil was drilled with an electric push-hammer (diameter 50 mm) and a hydraulic push machine which was used to survey the soil profile and to gather the sample. In general, 0-0.2/0.5 m drilling depth contained humus topsoil, 0.2-0.5 m had light-darker medium-coarse sand with changing amounts of gravel and stones. These samples had inconspicuous organoleptic characteristics. Drilling several locations, one contaminated site was detected. Under the humus topsoil and after a small sandy layer, a 10-15 cm thick dark-grey to black silty-sandy layer with smell of taroil was sampled. Beneath this layer, again inconspicuous sands were observed. In all sites, a MOSTAP-Sensor was used to determine the sum of high-volatile hydrocarbons in soil air.

2.3. *Sample preparation*

The most common method of preparing performance samples for VOCs is to spike a soil sample with a methanol based standard [16,17,36,37]. The working solution containing 12 target VOCs was prepared in 5 mL of ultra pure methanol at 1 mg/L (ppm). Spiked soil samples were prepared by placing approximately 5 g of soil in a pre-weighed 40 mL amber glass vial (EPA quality, Wheaton, Millville, NJ, USA) containing a clean magnetic stirring bar (cross shape). Then each soil sample was spiked with 25 µL of the methanolic solution by using a 25 µL-glass syringe (Hamilton, Reno, NV, USA) and was immediately capped with Teflon®-faced silicone septa. Smaller spiking volumes (5 µL) were reported by Hewitt [38] to provide more precise replicates compared with higher spiking volumes (0.1 mL) due to preventing from volatile losses when the spike reaches the exterior surface of the soil. The present spiked soil samples can be considered to approximate a freshly contaminated soil, not one that has been aged, because the sorption of VOCs by soil occurs over a period of months rather than hours [39]. In those time-consuming periods, when dealing with VOCs, uncontrolled losses are expected to happen and some target compounds with high volatility and degradability such as benzene can be completely lost [16]. After some degradation problems when storing at 4 ºC (see Results and discussion section) all samples were frozen (-15 ºC) until analysis.

2.4. Instrumentation

The 40 mL-vials were subsequently placed in a SOLATek 72 Multi-Matrix Vial Autosampler coupled to a Purge and Trap Concentrator Tekmar 3100 (both by Tekmar-Dohrmann, Mason, OH, USA). Both instruments are controlled by one easy-to-use package TekLink Software. This system permits the fully automated and reproducible analysis of VOCs in water and soil and is equipped with a magnetic stirrer and temperature control. In contrast to liquid samples, solids are purged directly in the vial and the purge gas transfers the VOCs towards the trap of the concentrator. Fifteen mL of organic-free water were introduced from a pressurized tank by means of the robotic needle into the vial by penetrating its septum. This volume was selected to guarantee the total coverage of the soil sample and contained the IS solution (at final concentration of 1 µg/kg). The sample was heated to pre-selected temperature (from 30 to 80 ºC) and held this temperature for 1 minute (sample preheat time to reach equilibrium) before commencing the purge process. During this time and the purge time the mixture was magnetically stirred. Following, the sample was purged with helium at 40 mL/min for 13 minutes. It was reported in the literature that stirring the soil sample prior to and during the purge step gave improved extraction efficiencies and slightly larger relative standard deviations [37,40]. VOCs were absorbed onto a Tenax-silica gel-charcoal trap (Supelco, Bellefonte, PA, USA) kept at room temperature (20 ºC). After sample loading, the trapped sample components were desorbed at 225 ºC during 4 minutes and transferred directly to the GC/MS system.

A Trace GC coupled to a Voyager MS (ThermoQuest Finnigan, Austin, TX, USA) was used. Extracts were transferred onto a 75 m x 0.53 mm i.d. DB-624 (J&W Scientific, Folsom, CA, USA) fused silica capillary column with a 3-µm film thickness. The MS was operated in electron impact (EI) mode at 70eV. Specific GC/MS parameters for target compounds can be found elsewhere [11,41,42]. In the same way, peak detection and integration were also carried out by use of XCalibur software (version 1.2, GC/MS) and quantitation was performed by automated XCalibur Quantitative Analysis by Internal Standard Calibration.

3. Results and Discussion

3.1. Effect of purge temperature and water influence

Method optimization was principally focussed on the selection of the best purge temperature for the simultaneous analysis of several chemical families of gasoline additives in solid samples. This fully closed-system purge and trap is indicated for VOCs that have boiling points below 200 ºC and that are insoluble or slightly soluble in water. But it is mentioned that the purging efficiency can be improved for water soluble analytes (e.g. ketones and alcohols) when purging at an elevated temperature of 80 ºC as compared to 20 ºC or 40 ºC [29]. Table 1 reports the boiling points (Bp) of target compounds which ranged from 55 to 170 ºC, the solubility in water and the Henry's law constant (Hc) which rules the purging efficiency of VOCs. Given the widespread levels varying from 9.05E-06 to 6.25E-02 (atm·m^3)/(g·mol), the mixture contained in the vial (5 g of spiked soil plus 15 mL of organic-free water including 5 µL of 1 mg/L methanolic solution of IS) was heated at different purging temperatures and magnetically stirred to effectively recover all target analytes.

Preliminary testing at 30, 40, 60 and 80 ºC was performed by analysing 2 replicates of spiked water samples without soil and 5 replicates of spiked raw Ebro river basin sediments; both at the same level (5 µg/kg corresponding to 1.67 µg/L in aqueous matrix). Some BTEX losses were detected when the raw sediments were spiked and immediately stored at 4 ºC until analysis which was attributed to biodegradation processes (see *Effects of storage conditions section*). However, some results were extracted from spiked water samples as shown in Table 1. A value of 100 was assigned to the maximum peak area for each compound and the rest of the areas were correlated to this value. In all cases, better efficiencies were obtained at low temperatures (30 or 40 ºC) in comparison to high temperatures (60 ºC or 80 ºC). For TBA, no peak was detected above 40 ºC, due to its high solubility in water, and lowest Hc. At purging temperatures of 60 and 80 ºC, losses of compounds with low Bp and Hc occurred. At these conditions, a good correlation was found between Bp and Hc and percentage recovery (R^2=0.61 and 0.84, at 60 and 80 ºC, respectively for Bp and R^2=0.39 and 0.58, at 60 and 80 ºC, respectively for Hc, excluding in this latter correlation DCPD which had highest values and was considered as outlier). Thus, all fuel oxygenates plus benzene (lowest Bp and Hc) were lost or partly lost at purging temperatures starting at 60 ºC, close to their Bp. These compounds exhibit, in addition, highest solubility. In fact, an excellent negative correlation was found between the logarithm of the solubility (performed to cluster the data) and extraction efficiencies (R^2=0.62 and 0.86, at 60 and 80 ºC, respectively), with most soluble compounds yielding lower extraction recoveries. The study was further optimized by testing purge temperatures closer to 40 ºC (35 ºC and 50 ºC) and using non-biologically active or inert substrates to avoid the potential degradation problems. Freeze-dried and homogenized Ebro river basin sediments were tested and satisfactory results were obtained (see relative values in Table 1). The same trend as in water samples was observed in sediments, but now it was clear that the extractions of target compounds slightly increased with the temperature and then reached a maximum at 35 ºC or 40 ºC to fall off with higher temperatures. Only DCPD needed 50 ºC to get the best extraction possibly because of its higher boiling point. These results fitted with the ones found in the literature. According to Charles and Simmons [43], the performance of sediment P&T methods are primarily dependent on the physico-chemical properties of the analytes, rather than intrinsic properties of the sediments. In this direction, Bianchi et al. [24] suggested better correlation between the recoveries of 60 VOCs (at 60 ºC) and their boiling points than related to vapour pressure or aqueous solubility, but significantly dependent upon organic compound class. In fact, the addition of water to the soil sample was found to improve extraction yields and a significant increase in the chromatographic signals in comparison to dry soil extraction in several HS-SPME works [15,16,20]. Water displaces the analytes from the active sites in the soil, the pollutants compete with water molecules for the adsorption sites, and non-polar organic molecules are desorbed [30] and then released into the gas phase. However, the comparison data at 40 ºC and 80 ºC showed that signals increased in the absence of water while at 80 ºC the response decreased in its presence [15].

The retention times of the compounds which eluted at the beginning of the chromatogram (especially TBA) were affected by the raise of purge temperature (increase up to 1 minute at 80 ºC) and produced significant peak broadening. At elevated purging temperature, the target compounds are purged out of the solution but also significant amount of water vapour too. The water vapour will significantly reduce the retention volumes of the target compounds on the P&T trap. Therefore, at high purging temperature, the target compounds very likely just break through the trap during the purging process. Water vapours will also broadening the peaks for the front part of the chromatogram. It suppresses the MS signal, and increases the baseline level and noise too. The impact will tend to be stronger with higher purging temperature and could also explain the decrease in the recovery of some compounds above 60 ºC rather than thermal degradation or following reaction with other analytes. Overall, 40 ºC was selected as optimal purge temperature for the majority of target compounds. However, as can be observed in the chromatogram from a freeze-dried urban soil sample spiked at 10 µg/kg at the optimised conditions (Fig. 1), TBA peak still suffers of elevated background noise thus increasing the limit of detection of this compound.

As usual in most P&T studies, the addition of salt was not studied, although Zuloaga et al. [26] observed that when the soil is present, the addition of sodium chloride (NaCl) diminished the VOCs recoveries.

3.2. Quality parameters of the method

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analysed with in a sequence. However, in SOLATek 72 Autosampler, all sampling is followed by a complete hot water (at 90 ºC) rinse of the systems pathway and multiple pressurized sweeps virtually eliminating cross-contamination. In addition, simultaneous to GC/MS acquisition, bake condition were programmed at 230 ºC during 10 minutes to clean the trap. Each analytical sequence included quality control standards and procedural blanks to check noise and background levels, possible carryover effects and to cover little retention time variations.

Special precautions should be taken to avoid random background levels from external contamination. The laboratory where volatile analysis is performed should be completely free of solvents and preferably, not subjected to car exhaust emissions. Stirring bars can be reused, provided that they are thoroughly cleaned between uses with Extran detergent (containing sodium hydroxide from Merck, Darmstadt, Germany) in an ultrasonic bath. In the same way, glass material was carefully washed and heated at 350 ºC overnight to eliminate residual organic matter.

The matrix effect was evaluated to establish the most adequate calibration and quantification mode. Although EPA method 5035A suggests that the calibration curves can be obtained by analysing blank water samples spiked with target compounds, in our study, some matrix effects were detected depending on the analyte. 5 g-urban freeze-dried soils were spiked with target compounds methanolic solution in a range from 0.05 to 40 µg/kg and 15 mL of organic-free water were added by the autosampler containing the IS solution at a final constant concentration of 1 µg/kg. The same procedure was adapted for water and 5 mL aqueous standards containing the target compounds at the same calibration levels as for soils and 10 mL of water and the IS were automatically added. External and internal standard calibration equations were obtained by applying linear regression in each data set.

The first observation was the lower response for most of the target compounds in spiked soils versus spiked waters. For example, the recoveries of soils spiked at 20 µg/kg were between 16 to 78% (Table 2) when external standard calibration using water as matrix was performed, with the exception of TBA which had always higher signal in soils likely influenced by background noise (Fig. 1). One of the lowest recoveries was found for benzene, as shown in Fig. 2a. External standard quantification is highly influenced by the type of matrix which affects extraction yields and can cause biased quantification. The use of IS and water calibration improved the linearity of benzene minimizing extraction errors and resolving matrix effects. Similarly, good correlation coefficients (R^2) were obtained using fluorobenzene and 1,2-dichlorobenzene-d_4 as IS for TBF (0.98), TAME (0.996), BTEX (0.97-0.997), TCE (0.9992) and DCPD (0.995); but they did not improve the ones from the rest of oxygenate ethers (TBA, MTBE and DIPE, which were more acceptable using external calibration, with R^2 from 0.98 to 0.990). In general, it can be observed that the use of these IS did not solve completely the matrix effects. In this case, quantification should be performed using a similar pre-treated (e.g. freeze dried or heated at 400 ºC in order to eliminate VOCs) soil matrix. Otherwise, the use of more specific IS for the analysis of TBA, MTBE and DIPE is recommended, such as some isotopic labelled target compound.

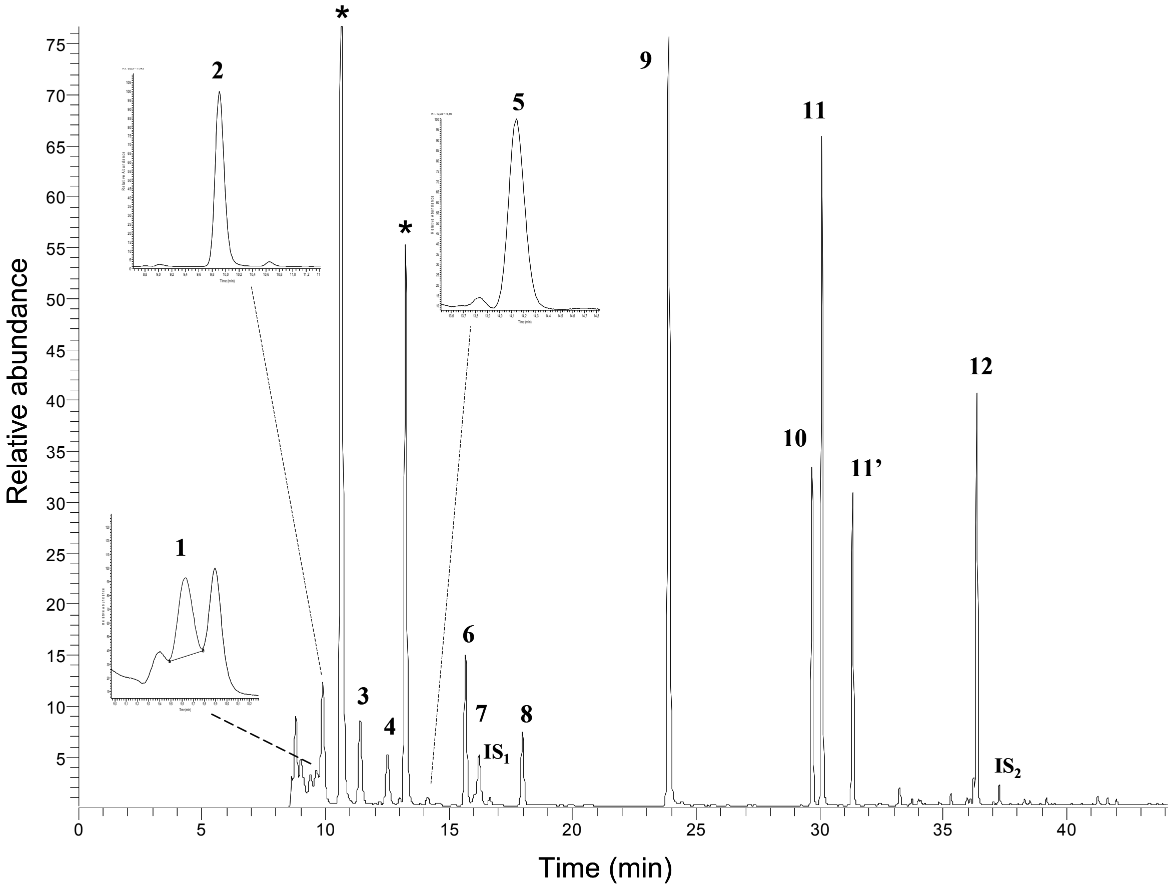

Fig. 1. Total ion chromatogram (TIC, 108) in selected ion monitoring (SIM) mode for a 10 μg/kg spiked urban soil at 40 ºC. Compound identification number: 1 = TBA (m/z = 59), 2 = MTBE (m/z = 73), 3 = DIPE, 4 = ETBE, 5 = TBF (m/z = 59), 6 = benzene, 7 = TAME, IS$_1$ = fluorobenzene, 8 = TCE, 9 = toluene, 10 = ethylbenzene, 11 = m+p-xylene, 11’ = o-xylene, 12 = DCPD and IS$_2$ = 1,2-dichlorobenzene-d$_4$. (*) Non-identified interferences

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Whereas the EPA and other multi-compound methods rely on the use of one or two generic IS, commonly fluorobenzene other studies claim the use of deuterated compounds ([$^{2}H_{10}$]TBA (TBA-d_{10}) or [$^{2}H_{3}$]MTBE (MTBE-d_3)) especially when matrix effects appear [44]. However, signal suppression induced by the matrix can lead to poor method relative recoveries, as found by Zwank et al. [45] using TBA-d_{10} and [$^{2}H_{6}$]benzene. In view of that situation, TAME was also suggested in their study as IS when its presence is not expected in the environmental samples instead of the more expensive deuterated compounds. Recently, Tanabe et al. [46] employed [$^{2}H_{12}$]MTBE (MTBE-d_{12}) instead of MTBE-d_3 because the presence of carbon bisulfide in the samples can interfere with the quantification of *m/z* 76. Despite these problems, the use of deuterated standards should be better suited than another unspecific IS.

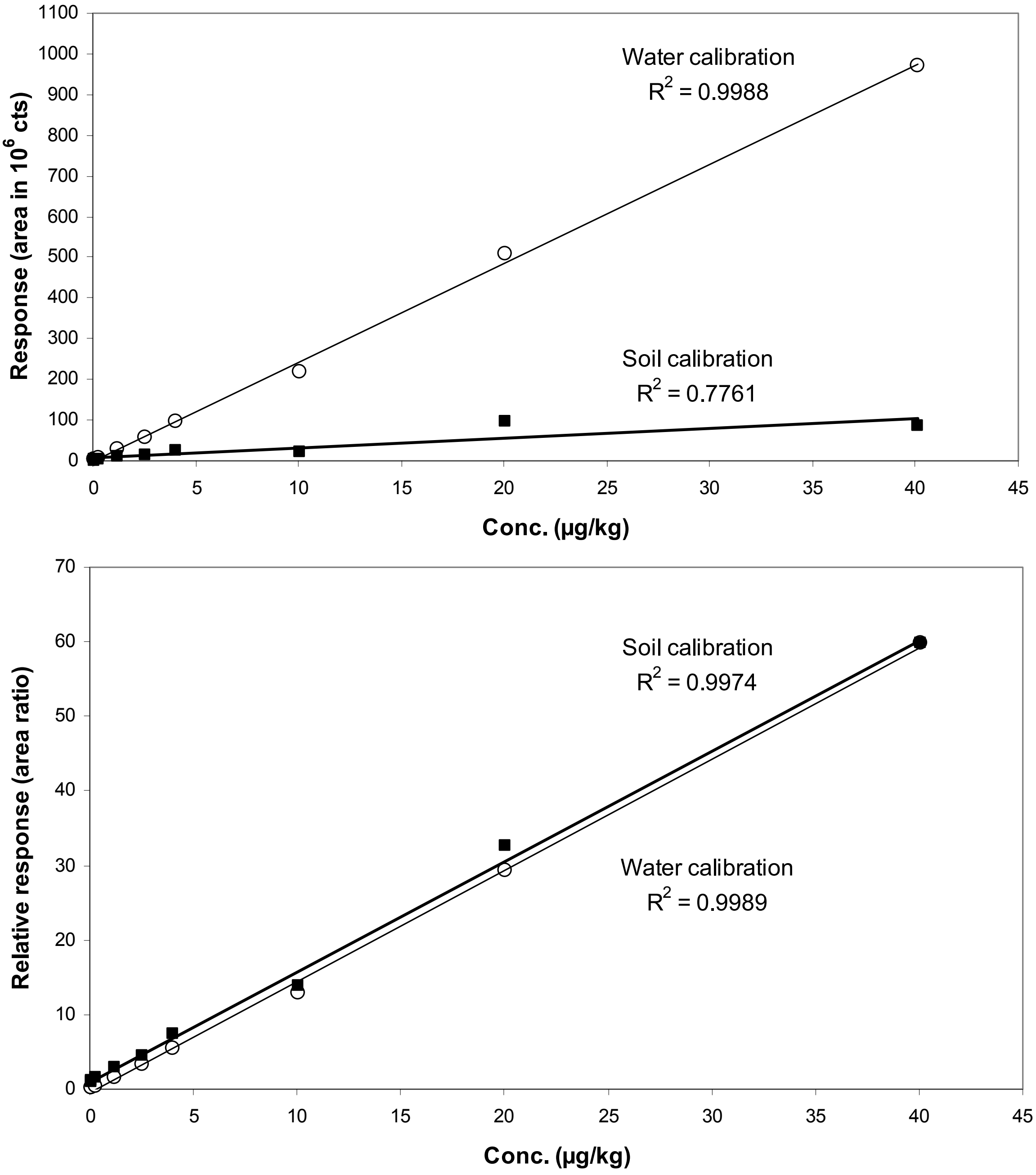

Fig. 2. Calibration of benzene over a concentration range of 0.05-40 µg/kg using water or soil spiked samples. (a) External standard calibration and (b) Internal standard calibration using fluorobenzene.

Moreover, it was demonstrated that the calibration performance using only water standards as EPA method is subjected to errors when multiresidue analysis is to be performed and thus, a similar matrix than the sample or even better a standard addition protocol is necessary for their accurate determination in solid samples.

Other quality parameters were tested and are included in Table 2. Method detection limits (MDLs) were calculated as the amount of analyte which gives a peak area response three times as great as the standard deviation of the response obtained from the blank according to Bianchi et al. [24]. In general, MDLs were in the sub-µg/kg levels comparable to HS-SPME [16,17]. Procedural blanks revealed the presence of MTBE, ETBE, DIPE, TBF, benzene, ethylbenzene, xylenes and TCE at amounts lower that the detection limit, specifically between 0.09 and 0.3 µg/kg. Short term precision or repeatability was expressed as the relative standard deviation (RSD) over five consecutive replicates (at 4 µg/kg) analysed in the same day and reproducibility over a period of three days (at 10 µg/kg). In both cases, the results are presented with and without IS correction. The repeatability did not vary when calculated with and without IS, but method precision was highly improved when using IS through several days. That fact may be explained for drifting ionization efficiencies when the instrument is running. On the whole, satisfactory RSD values were achieved (from 2 to 13%) although some punctual higher variations up to 24% were detected for TBA, DIPE or toluene.

3.3. Effects of storage conditions

Some BTEX losses were detected during optimization process when raw sediments were spiked and immediately stored at 4 ºC until analysis (less than 24 hours). Independently of the purge temperature selected for the experiment, aromatic hydrocarbons signal decreased linear or exponentially in each case resulting in half life times from 6 to 15 hours. This fact was likely attributed to biologically degradation, specially when rapid biodegradation of these aromatic compounds has been reported previously [29,47-49]. Hewitt [48] observed a substantial BTEX reduction (from 26% loss to complete benzene biodegradation) when spiked soils were stored at 4 ºC over 28-day holding period. For extremely biologically active soils this can occur in less than five days [47]. In addition, in laboratory-fortified matrices, target compounds are more readily available to soil microorganisms than soil experiencing long-term exposure where analytes can become trapped in micropores or other inaccessible or slow desorption sites [50].

An experiment to assess the effects of time and storage conditions was carried out. The goals of the study were to evaluate the stability of the target compounds at two temperatures (4 ºC and -15 ºC) and at different storage periods (up to 14 days), on 3 different preservation alternatives: empty vial without any additive, acidified with sodium bisulphate ($NaHSO_4$) and basified with trisodium phosphate dodecahydrate ($Na_3PO_4 \cdot 12H_2O$ or TSP).

Solutions were prepared in organic-free water at 20% (w/w) for the acid (pH<2) as recommended by EPA method (0.2 g of NaHSO4 per each soil sample g) and 1% (w/w) for the base (pH>10) and 5 mL were added to each vial containing 5g-spiked soil samples. Three replicates of each treatment were analysed, then average and SD were calculated.

The presence of a chemical preservative was found to affect the purging efficiencies of the analytes. For some target compounds such as TBA, MTBE or TAME higher response under acidic conditions was observed. This could be associated to the salting-out effect that enhanced the release of polar compounds to the headspace more than non-polar ones [16,51,52]. The ratio between sample response at and or 14 days (n=3) at each preservative condition was calculated to assess compound stability.

To study the effect of storage temperature on analyte stability, the percentage ratio of spiked soil samples without any preservative stored at 4 ºC and -15 ºC during 7 days was studied, as shown in Fig. 3. Although good stabilities (>91%) were obtained for TAME, TCE, DCPD and BTEX at both temperatures, more than 50% losses were observed when ETBE, DIPE or TBF were stored at 4 ºC. In fact, rapid loss of these compounds was detected within the first 48 hours of storage at 4 ºC.

Given the fact that best preservation was obtained when freezing, the effect of different preservation alternatives on the stability of each target compound was follow by the percentage ratios of spiked soil samples after 7 and 14 days under -15 ºC, as presented in Table 3. In general, although the concentration of target compounds decrease with time, some of them such as degradation products (TBA and TBF) can increase. For some analytes, the preservation alternative seem to be not so critical, this could be the case of MTBE or ETBE. But frequently the use of $NaHSO_4$ provided the lowest recoveries in most of BTEX (for instance, 50% of benzene after 14 days in front of 75% without additive or 81% using TSP), TAME or TCE.

Acid preservation of samples containing MTBE was suggested to be avoided when high temperatures are used (such as Methods 5021 (static headspace), 5030 (P&T) or 5032 (vacuum distillation)), which can cause degradation of this compound to TBA [29,53-55]. Under normal environmental conditions ethers do not undergo hydrolysis at significant rates without enzyme catalysis [8]. However, if the sample is heated, the acid commonly added in excess to preserve the sample (giving pH of between 1 and 2) can actually cause the hydrolysis of ether bonds [56]. For instance, Wade [56] reported evidence of decreasing MTBE concentrations in 91 acidified groundwater samples and O’Reilly [54] measured the rate of MTBE hydrolysis at 26 ºC and 37 ºC. Consequently, Kovacs [57] developed an alternative procedure using a base (TSP) to obtain a pH greater than 11 which showed no evidence of MTBE hydrolysis to TBA.

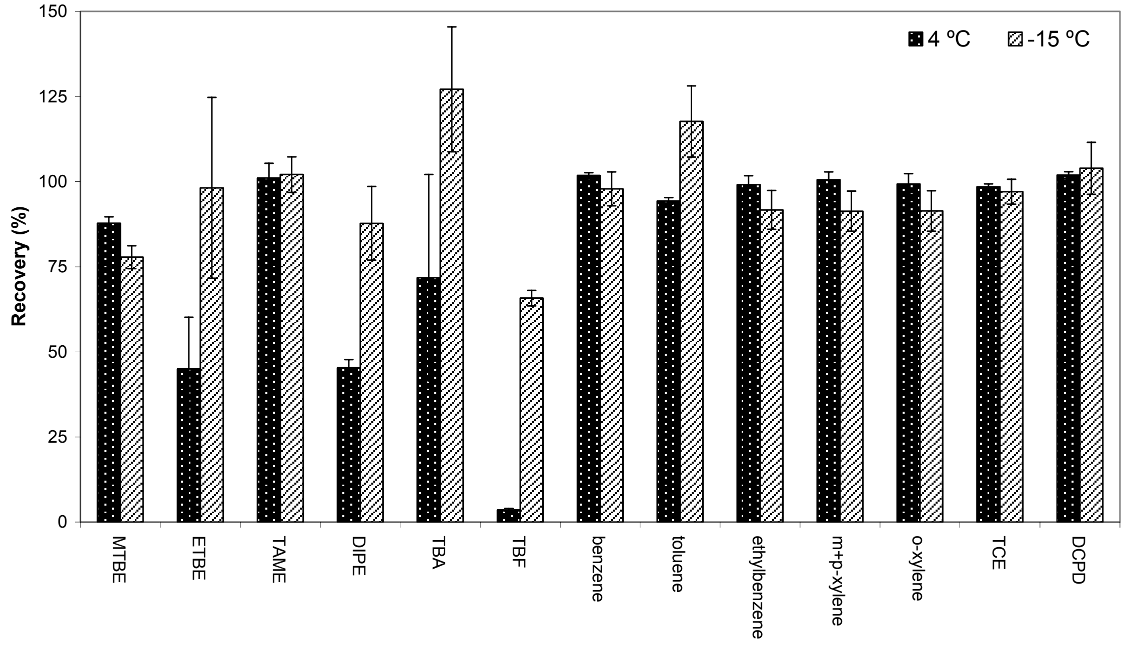

Fig. 3. Short-term effect of temperature storage (4 ºC and -15 ºC) on the stability of each analyte (expressed as average ratio % and standard deviation of three replicates) in spiked freeze-dried urban soil samples (10 µg/kg) without any preservative after 7 days of storage.

However, although TBA is not subject to hydrolysis because it lacks a leaving group and an appropriate site for nucleophilic attack [58-60], TBF contains an ester linkage that can be hydrolyzed to TBA and formic acid [58,59] in acidic also in basic conditions [8]. In the present study, MTBE recoveries under acid conditions were not found appreciably lower to prove the hydrolysis previously mentioned in the literature. TBF recoveries showed very high variability among preservation alternatives. When TBF was stored under basic conditions, very low recoveries were obtained (up to 25%); whereas greater than 180% were measured under acid preservation. However, these changes seemed not to be reflected in TBA responses, taking into account that TBF hydrolysis as well as MTBE/ETBE degradation should result in nearly stoichiometric TBA accumulation. Although TBA recoveries exceeded 120% in all preservation alternatives, they can not be completely explained by parental compounds degradation. Perhaps the production of other degradation products (*tert*-amyl alcohol (TAA), 2-methoxy-2-methyl propionaldehyde (MMP), acetone, methyl acetate, isobutene, hydroxyisobutyraldehyde (HIBA) and formaldehyde [61,62]) with low masses may coelute with TBA or TBF peaks which in turn present low MS response (refer to Fig.1).

Other disadvantages related to the use of $NaHSO_4$ are the potential effervescence in samples containing carbonates which may result in loss of volatile compounds or the corrosive vapours which can create active sites on the trapping material of the instrument [29].

Overall, some advices can be pointed out from this preliminary experiment: (i) soil samples should be analysed as soon as possible after collection, stored under -15 ºC for not longer than 7 days if degradation products have to be analyzed; (ii) the non-preservative alternative (empty vial) provided good recoveries of the most analytes when freezing the samples, however if active biologically soil are analysed the preservation with NaHSO4 should be avoided and the use of TSP is strongly recommended.

3.4. Sampling and analysis of environmental soils

A preliminary screening sampling campaign has been carried out in a suspected gas contaminated site, close to a gasoline station and in a high traffic road area. The installation of monitoring wells permitted to sample 9 soils in depth (> 0.5-2.5 m) plus 3 surface samples. A total of 24 sandy soil samples were taken with Terra Core samplers which provided a mean of 5.1 ± 0.7 g. All samples were collected in duplicate approximately 20 cm apart and the reported value is the mean of these two samples. In our precise sampling protocol, once collected, the samples are directly transferred from the Terra Core samples to a pre-weighed 40 ml amber vial containing the clean stirring bar, which is weighed again upon arrival to the laboratory. So the vial is never opened and no sample manipulation can lead to losses of target compounds. Samples were preserved using the empty vial condition and were analyzed within one week. Using the protocol depicted above and water calibration using internal standard quantification, the standard deviation of the internal standards fluorobenzene and 1,2-dichlorobenzene-d_4, added at 0.6 µg/kg was of 14 and 35%, respectively and the recovery was of 104% and 91% respectively.

Table 4 indicates the threshold and point source levels in deep samples collected in an abandoned gas work station and levels in 3 surface soil samples collected in different places. BTEX, TBA and TCE were the only compounds detected. BTEX were present at low levels in surface samples, with the prevalence of benzene and toluene in samples close to the gasoline station of traffic road. Contrarily, toluene, ethylbenzene and xylenes were present at concentration higher than 2700 µg/kg wet weight (ww) in the deep contaminated sample while benzene was only present at 75 µg/kg ww, due to its higher degradability. TBA was the only compound detected in deep non-contaminated soil at a mean concentration of 3.42 µg/kg.

Similar results were reported by Moreels et al. [63] in Belgian soils. Whereas any of the fuel additives were detected above the detection limits (3 µg/kg) in garden top soils never exposed to gasoline point sources, higher concentrations of MTBE and BTEX were found in deep soils close to petrol stations or garages showing a wide range of magnitudes (from 5 µg/kg to 5,000 mg/kg). In most cases, benzene exhibited the lower level (3-18% of the total fuel contamination).

We used the MDL as the reporting levels of target compounds (Table 2) and positive samples were reported provided they were present in both duplicates. The standard deviation of duplicate analysis was from 0.02 to 0.5, indicating a good reproducibility of both the sampling and analytical procedures. This pilot monitoring campaigns serves prove the efficiency of the method which in turns permits to set the concentration ranges of several gasoline additives in impacted areas and in samples known not to be influenced by point sources.

4. Conclusions

A closed-system P&T-GC/MS using a SOLATek 72 Multi-Matrix Vial Autosampler has proven to be a robust, fully automated and reliable methodology for the analysis of gasoline additives in solid samples at µg/kg levels. Optimal purge temperature was 40 ºC for the majority of target compounds, even for the most water soluble analytes (MTBE and main degradation products, TBA and TBF). Satisfactory method precision (from 2 to 13%) was achieved and highly improved by the use of IS quantification and sample responses were stable through several days, with the exception of some punctual higher variations up to 24% for TBA, DIPE or toluene.

As far as matrix effects were detected for the most gasoline additives, calibration performance using only water standards and generic IS is not suitable and thus, a standard addition protocol is recommended for their accurate analysis in solid samples.

Regarding sample preservation techniques, the use of NaHSO4 provided the lowest recoveries in most of BTEX compounds, TAME or TCE. 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 active biologically soil are analysed the preservation with TSP is strongly recommended.

The present study also provides some useful/practical recommendations (about IS use, sampling devices and storage conditions) for the future application on real samples in current monitoring programs at gasoline pollution risk sites where up to now little monitoring data for MTBE in soils in Europe are available.

Acknowledgments

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References

[1] A.D. Hewitt, K.F. Myers, Sampling and On-Site Analytical Methods for Volatiles in Soil and Groundwater: Field Guidance Manual, US Army Corps of Engineers, Cold Regions Research & Engineering Laboratory,

Washington, DC, Special Report 99-16, 1999.

[2] R. Johnson, J. Pankow, D. Bender, C. Price, J. Zogorski, Environ. Sci. Technol. 34 (2000) 210A.

[3] T.C. Schmidt, E. Morgenroth, M. Schirmer, M. Effenberger, S.B. Haderlein, in A.F. Diaz, D.L. Drogos (Editors), Oxygenates in Gasoline: Environmental Aspects, Washington, DC, 2002, p. 58.

[4] R. Ahlberg, J.P. Gennart, R.E. Mitchell, E. Schulte-Koerne, M.E. Thomas, H. Vahervuori, H. Vrijhof, C.D. Watts, An environmental risk assessment of MTBE use in Europe, EFOA/ECETOC Task Force on Environmental Risk Assessment of MTBE, Brussels, 2001.

[5] P.J. Squillace, J.F. Pankow, N.E. Korte, J.S. Zogorski, Environ. Toxicol. Chem. 16 (1997) 1836.

[6] American Petroleum Institute, A Guide to the Assessment and Remediation of Underground Petroleum Releases, Washington, DC, 1996.

[7] J.M. Davidson, D.N. Creek, Environ. Forensics 1 (2000) 31.

[8] C.D. Church, J.F. Pankow, P.G. Tratnyek, Environ. Toxicol. Chem. 18 (1999) 2789.

[9] P. Ellis, in L.U.S.T.Line, New England Interstate Water Pollution Control Commission, Lowell, MA, 2001, p. 17.

[10] J. Dottridge, M. Hall, S. Firth, A Review of Current MTBE Usage and Occurrence in Groundwater in England and Wales, Environment Agency, Bristol, Research and Development Technical Report P406, 2000.

[11] M. Rosell, S. Lacorte, C. Forner, H.P. Rohns, R. Irmscher, D. Barcelo, Environ. Toxicol. Chem. 24 (2005) 2785.

[12] A. Fischer, C. Oehm, M. Selle, P. Werner, Environ. Sci. Pollut. 12 (2005) 381.

[13] E. Frye, Summary report on a survey of state experiences with MTBE and other oxygenate contamination at LUST sites, New England Interstate Water Pollution Control Commission, Lowell, MA, 2003.

[14] US Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Washington, DC, EPA SW-846, 3rd edition, 1996.

[15] P. Pastore, G. Favaro, D. Badocco, I. Lavagnini, Ann. Chim-Rome 95 (2005) 741.

[16] M. Llompart, K. Li, M. Fingas, Talanta 48 (1999) 451.

[17] O. Ezquerro, G. Ortiz, B. Pons, M.T. Tena, J. Chromatogr. A 1035 (2004) 17.

[18] Accelerated Solvent Extraction (ASE) of hydrocarbon contaminants (BTEX, Diesel, and TPH) in soils. Application Note 324, Dionex, Sunnyvale, CA, 1997.

[19] M. Ojala, I. Mattila, T. Sarme, R.A. Ketola, T. Kotiaho, Analyst 124 (1999) 1421.

[20] M. Ojala, I. Mattila, V. Tarkiainen, T. Sarme, R.A. Ketola, A. Maattanen, R. Kostiainen, T. Kotiaho, Anal. Chem. 73 (2001) 3624.

[21] US Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Department of Commerce, National Technical Information Service, Washington, DC, EPA SW-846, 3rd edition, 1986.

[22] T. Bellar, Measurement of volatile organic compounds in soils using modified purge-and-trap and capillary gas chromatography/mass spectrometry, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, 1991.

[23] A. Bianchi, M.S. Varney, J. High Res. Chromatogr. 12 (1989) 184.

[24] A.P. Bianchi, M.S. Varney, J. Phillips, J. Chromatogr. 542 (1991) 413.

[25] O.C. Amaral, L. Olivella, J.O. Grimalt, J. Albaiges, J. Chromatogr. A 675 (1994) 177.

[26] O. Zuloaga, N. Etxebarria, L.A. Fernandez, J.M. Madariaga, Anal. Chim. Acta 416 (2000) 43.

[27] N. Campillo, P. Vinas, I. Lopez-Garcia, N. Aguinaga, M. Hernandez-Cordoba, Talanta 64 (2004) 584.

[28] US Environmental Protection Agency, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Washington, DC, EPA Method 5035, Revision 0, 1996.

[29] US Environmental Protection Agency, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Office of Solid Waste and Emergency Response, Washington, DC, EPA Method 5035A, Draft Revision 1, 2002.

[30] J. Ruiz, R. Bilbao, M.B. Murillo, Environ. Sci. Technol. 32 (1998) 1079.

[31] R.L. Siegrist, Abstr. Pap. Am. Chem. S. 200 (1990) 33.

[32] A.D. Hewitt, Environ. Sci. Technol. 32 (1998) 143.

[33] S.S. Sorini, J.F. Schabron, J.F. Rovani, Soil Sediment Contam. 11 (2002) 19.

[34] S.S. Sorini, J.F. Schabron, J.F. Rovani, J. Test. Eval. 31 (2003) 247.

[35] J.S. Alvarado, C. Rose, Talanta 62 (2004) 17.

[36] B.A. Schumacher, S.E. Ward, Environ. Sci. Technol. 31 (1997) 2287.

[37] M.W. Couch, C.J. Schmidt, S.C. Wasdo, Adv. Environ. Res. 4 (2000) 97.

[38] A.D. Hewitt, Storage and preservation of soil samples for volatile organic compound analysis, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, CRREL Special Report, 99-5, 1999.

[39] J.J. Pignatello, B.S. Xing, Environ. Sci. Technol. 30 (1996) 1.

[40] S.C. Wasdo, J. Kancler, M.W. Couch, C.J. Schmidt, Adv. Environ. Res. 3 (1999) 352.

[41] S. Lacorte, L. Olivella, M. Rosell, M. Figueras, A. Ginebreda, D. Barcelo, Chromatographia 56 (2002) 739.

[42] M. Rosell, S. Lacorte, A. Ginebreda, D. Barcelo, J. Chromatogr. A 995 (2003) 171.

[43] M.J. Charles, M.S. Simmons, Anal. Chem. 59 (1987) 1217.

[44] P. Dewsbury, S.F. Thornton, D.N. Lerner, Environ. Sci. Technol. 37 (2003) 1392.

[45] L. Zwank, T.C. Schmidt, S.B. Haderlein, M. Berg, Environ. Sci. Technol. 36 (2002) 2054.

[46] A. Tanabe, Y. Tsuchida, T. Ibaraki, K. Kawata, A. Yasuhara, T. Shibamoto, J. Chromatogr. A 1066 (2005) 159.

[47] A.D. Hewitt, Proceedings of the 11th Annual Waste Testing and Quality Assurance Symposium. Washington, DC, 1995, p. 173.

[48] A.D. Hewitt, Environ. Sci. Technol. 31 (1997) 67.

[49] S.S. Sorini, J.F. Schabron, Proceedings of the 15th Annual Waste Testing and Quality Assurance Symposium. Arlington, VA, 1999, p. 129.

[50] S.M. Steinberg, J.J. Pignatello, B.L. Sawhney, Environ. Sci. Technol. 21 (1987) 1201.

[51] B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography. Theory and Practice, Wiley-VHC, New York, 1997.

[52] Z.E. Penton, in P.R. Brown, E. Grushka (Editors), Advances in Chromatography, Marcel Dekker, New York, 1997.

[53] H. White, B. Lesnik, J. Wilson, in L.U.S.T.Line, New England Interstate Water Pollution Control Commission, Lowell, MA, 2002, p. 1.

[54] K.T. O'Reilly, M.E. Moir, C.D. Taylor, C.A. Smith, M.R. Hyman, Environ. Sci. Technol. 35 (2001) 3954.

[55] P.W. McLoughlin, R.J. Pirkle, D. Fine, J.T. Wilson, Ground Water Monit. R. 24 (2004) 57.

[56] M.J. Wade, Abstr. Pap. Am. Chem. S. 216 (1998) U789.

[57] D.A. Kovacs, D.H. Kampbell, Arch. Environ. Con. Tox. 36 (1999) 242.

[58] T. Mill, Environ. Toxicol. Chem. 1 (1982) 135.

[59] J.C. Harris, in W.J. Lyman, W.F. Reehl, D.H. Rosenblatt (Editors), Handbook of Chemical Property Estimation Methods, McGraw-Hill, New York, 1982, p. 7.1.

[60] R.A. Larson, E.J. Weber, in Reaction Mechanisms in Environmental Organic Chemistry, Lewis, Chelsea, MI, 1994, p. 103.

[61] J.L. Acero, S.B. Haderlein, T.C. Schmidt, M.J.F. Suter, U. Von Gunten, Environ. Sci. Technol. 35 (2001) 4252.

[62] A. Aguera, M. Mezcua, D. Hernando, S. Malato, J. Caceres, A. Fernandez-Alba, Intern. J. Environ. Anal. Chem. 84 (2004) 149.

[63] D. Moreels, L. Bastiaens, F. Ollevier, R. Merckx, L. Diels, D. Springael, FEMS Microbiol. Ecol. 49 (2004) 121.

TABLES

Table 1. Effect on the relative response of each analyte (expressed as relative area counts %) by varying the purge temperature in 15 mL spiked water (n=2) and spiked freeze-dried Ebro river basin sediments (n=5). All samples spiked at the same concentration (5 µg/kg corresponding to 1.67 µg/L in aqueous matrix) for all the analytes. Boiling point (Bp), Henry's Law constant (Hc) and solubility in water at 25 ºC of target compounds are provided.

					Spiked water (n=2)				Spiked sediments (n=5)				
Compound	Acronym	Bp (ºC)^{a}	Hc (atm·m^{3})/ (g·mol)^{a}	Solubility (mg/L)^{a}	30 ºC	40 ºC	60 ºC	80 ºC	30 ºC	35 ºC	40 ºC	50 ºC	80 ºC
FUEL OXYGENATES													
methyl *tert*-butyl ether	MTBE	55	5.87E-04	51,000	100	91	53	32	70	100	94	67	31
ethyl *tert*-butyl ether	ETBE	73	1.39E-03	12,000	98	100	35	22	86	100	95	98	38
tert-amyl methyl ether	TAME	86	2.68E-03	2,640	84	100	67	43	81	97	100	98	53
diisopropyl ether	DIPE	69	2.28E-03	8,800	100	97	29	21	97	100	89	90	41
DEGRADATION PRODUCTS													
tert-butyl alcohol	TBA	82	9.05E-06	1,000,000	81	100	nd	nd	100	87	100	27	36
tert-butyl formate	TBF	83	6.90E-04	11,200	83	100	66	34	90	100	100	94	53
AROMATIC HYDROCARBONS													
benzene	B	80	5.55E-03	1,790	100	93	63	43	92	100	94	85	36
toluene	T	111	6.64E-03	526	100	98	72	57	90	100	100	98	96
ethylbenzene	E	136	7.88E-03	169	97	100	78	66	87	96	100	96	60
m+*p*-xylene	X	138-139	7.18E-03 6.90E-03	161-162	99	100	82	70	91	98	100	98	63
o-xylene		144	5.18E-03	178	96	100	80	68	85	94	100	99	65
OTHER VOCs													
trichloroethylene	TCE	87	9.85E-03	1,280	100	99	69	51	92	100	95	82	40
dicyclopentadiene	DCPD	170	6.25E-02	27	96	100	82	71	82	88	98	100	77

[a] Data obtained from: Syracuse Research Corporation PhysProp Database (www.syrres.com/esc/physdemo.htm).

Table 2. Quality parameters obtained by closed-system PT-GC/MS in SIM mode at 40 ºC: method detection limits (MDLs), recoveries, repeatability and reproducibility at different spiking levels using external and internal standard (IS) quantification.

Compound	MDLs (µg/kg) water	MDLs (µg/kg) soils	Recovery (%)[a] At 20 µg/kg without IS	Recovery (%)[a] At 20 µg/kg with IS	Repeatability (RSD %) At 4 µg/kg (n=5) without IS	Repeatability (RSD %) At 4 µg/kg (n=5) with IS	Reproducibility (RSD %) At 10 µg/kg (n=5) without IS	Reproducibility (RSD %) At 10 µg/kg (n=5) with IS
FUEL OXYGENATES								
MTBE	0.12	0.13	71	>150	4	8	11	6
ETBE	0.05	0.49	25	147	11	5	8	2
TAME	0.01	0.06	23	134	3	9	12	6
DIPE	0.06	0.41	68	>150	29	23	7	2
DEGRADATION PRODUCTS								
TBA	1.44	1.36	>150	>150	4	10	20	24
TBF	0.25	1.20	16	92	11	7	18	13
AROMATIC HYDROCARBONS								
benzene	0.04	0.33	19	111	5	8	14	9
toluene	0.34	1.63	75	144	11	13	15	20
ethylbenzene	0.14	1.26	65	124	7	7	13	4
m+*p*-xylene	0.15	1.51	73	140	11	12	15	6
o-xylene	0.11	1.20	60	116	10	11	13	4
OTHER VOCs								
TCE	0.08	0.70	22	126	6	8	13	8
DCPD	0.03	0.02	78	150	5	4	11	4

[a] The recoveries were calculated using the spiked water calibration curve.

Table 3. Effect of different preservation alternatives ($NaHSO_4$, TPS and non-preservative) on the stability of each analyte (expressed as average ratio % and standard deviation in brackets of three replicates) in spiked freeze-dried urban soil samples (at 10 µg/kg) after 7 and 14 days of storage under -15 ºC.

Compound	Non-preservative (empty vial) 7 days	Non-preservative (empty vial) 14 days	Acidic ($NaHSO_4$) 7 days	Acidic ($NaHSO_4$) 14 days	Basic (Na_3PO_4 or TPS) 7 days	Basic (Na_3PO_4 or TPS) 14 days
FUEL OXYGENATES						
MTBE	78 (3)	77 (4)	74 (2)	73 (7)	77 (2)	95 (1)
ETBE	98 (27)	121 (13)	115 (22)	113 (12)	103 (28)	128 (13)
TAME	102 (5)	75 (4)	85 (3)	59 (12)	91 (3)	82 (5)
DIPE	88 (11)	128 (10)	97 (20)	143 (28)	110 (4)	139 (7)
DEGRADATION PRODUCTS						
TBA	127 (18)	> 150 (70)	125 (12)	> 150 (10)	122 (8)	> 150 (21)
TBF	66 (2)	72 (4)	> 150 (58)	> 150 (77)	11 (1)	25 (7)
AROMATIC HYDROCARBONS						
benzene	98 (5)	75 (5)	79 (4)	50 (16)	99 (5)	81 (7)
toluene	118 (5)	111 (3)	131 (7)	127 (2)	128 (2)	124 (3)
ethylbenzene	92 (6)	73 (6)	70 (5)	56 (15)	97 (8)	102 (10)
m+*p*-xylene	91 (6)	73 (6)	79 (5)	60 (14)	101 (8)	108 (10)
o-xylene	91 (6)	73 (6)	79 (4)	62 (13)	98 (6)	102 (8)
OTHER VOCs						
TCE	97 (4)	78 (3)	69 (4)	52 (15)	93 (8)	83 (12)
DCPD	104 (8)	84 (6)	62 (48)	89 (52)	111 (4)	99 (6)

Table 4. Concentration in µg/kg and standard deviation of duplicate samples (in brackets) and number of detected samples out of 12 analyzed of target compounds in deep samples (8 non-contaminated and 1 contaminated) and in 3 surface samples (non-contaminated, gasoline station, traffic road).

	Deep soils		Surface samples		
Compound	Non-contaminated	Contaminated	Non-contaminated	Gasoline station	Traffic road
FUEL OXYGENATES					
MTBE	n.d.	n.d.	n.d.	n.d.	n.d.
ETBE	n.d.	n.d.	n.d.	n.d.	n.d.
TAME	n.d.	n.d.	n.d.	n.d.	n.d.
DIPE	n.d.	n.d.	n.d.	n.d.	n.d.
DEGRADATION PRODUCTS					
TBA	3.42 (0.08), n=7	n.d.	n.d.	n.d.	n.d.
TBF	n.d.	n.d.	n.d.	n.d.	n.d.
AROMATIC HYDROCARBONS					
benzene	n.d.	75 (5), n=1	0.48 (0.08), n=1	0.11 (0.05), n=1	0.21 (0.06), n=1
toluene	n.d.	> 6000, n=1	n.d.	12 (2.7), n=1	31 (2.7), n=1
ethylbenzene	n.d.	> 2700, n=1	n.d.	n.d.	n.d.
m+*p*-xylene	n.d.	>3000, n=1	2.7 (0.07), n=1	n.d.	n.d.
o-xylene	n.d.	>4200, n=1	2.7 (0.5), n=1	n.d.	n.d.
OTHER VOCs					
TCE	n.d.	0.9 (0.03), n=1	n.d.	n.d.	n.d.
DCPD	n.d.	n.d.	n.d.	n.d.	n.d.

3.3 DISCUSSIÓ DELS RESULTATS

L'**Art. 5** demostra com el mètode desenvolupat amb P&T-GC/MS és robust i fiable (precisió general entre 2-13%) per a la determinació dels 12 additius de la gasolina a concentracions prou baixes en sòls (LODs entre 0,02-1,63 µg/kg) com per a la seva aplicació a nivells ambientals.

La temperatura òptima de purga es va trobar a 40 ºC, per a la majoria d'analits. Tot i això, en el cas dels additius de la gasolina ens trobem davant de varies famílies químiques amb propietats físico-químiques molt diferents que fa que el mètode per extreure'ls no sigui òptim per a tots ells. L'eficiència de la purga a diferents temperatures s'ha pogut correlacionar amb els paràmetres físico-químics dels compostos estudiats. A temperatures superiors a 60 ºC s'han observat pèrdues dels compostos de més baix punt d'ebullició (Bp) i baixa constant de Henry (Hc). A més, els compostos més solubles es purguen amb més dificultat que els insolubles. Quan s'han representat les recuperacions relatives d'aquests (%) a diferents temperatures de purga envers les seves diferents propietats s'ha observat un progressiu augment del coeficient de correlació (R^2), que ha estat màxim a 80 ºC. Degut a les limitacions d'espai a les publicacions en revistes científiques, els gràfics no es troben inclosos a l'**Art. 5**. A la *Figura 21* es presenten les correlacions de les recuperacions a 60 i 80 ºC pel logaritme de la solubilitat (*A*), el Bp (*B*) i la Hc (*C*), totes elles inclouen tots els compostos d'estudi a excepció de la última que exclou el DCPD, que diferia massa de la resta.

En mostres sòlides, degut a l'aparició d'efectes matriu i major interferència del vapor d'aigua a temperatures elevades, l'ús de patrons interns adients es fa més necessari que no pas en aigües per a una bona quantificació dels compostos.

L'**Art. 5** ofereix les recomanacions pràctiques necessàries per a la minimització de les pèrdues volàtils dels compostos durant la presa, transport i emmagatzematge de les mostres sòlides. La tècnica de no-preservació química (vial buit) ofereix bones recuperacions quan les mostres són congelades (-15 ºC) i analitzades fins al cap de 7 dies. Quan s'esperin mostres biològicament actives, la preservació a pH bàsic es preferible a la de pH àcid.

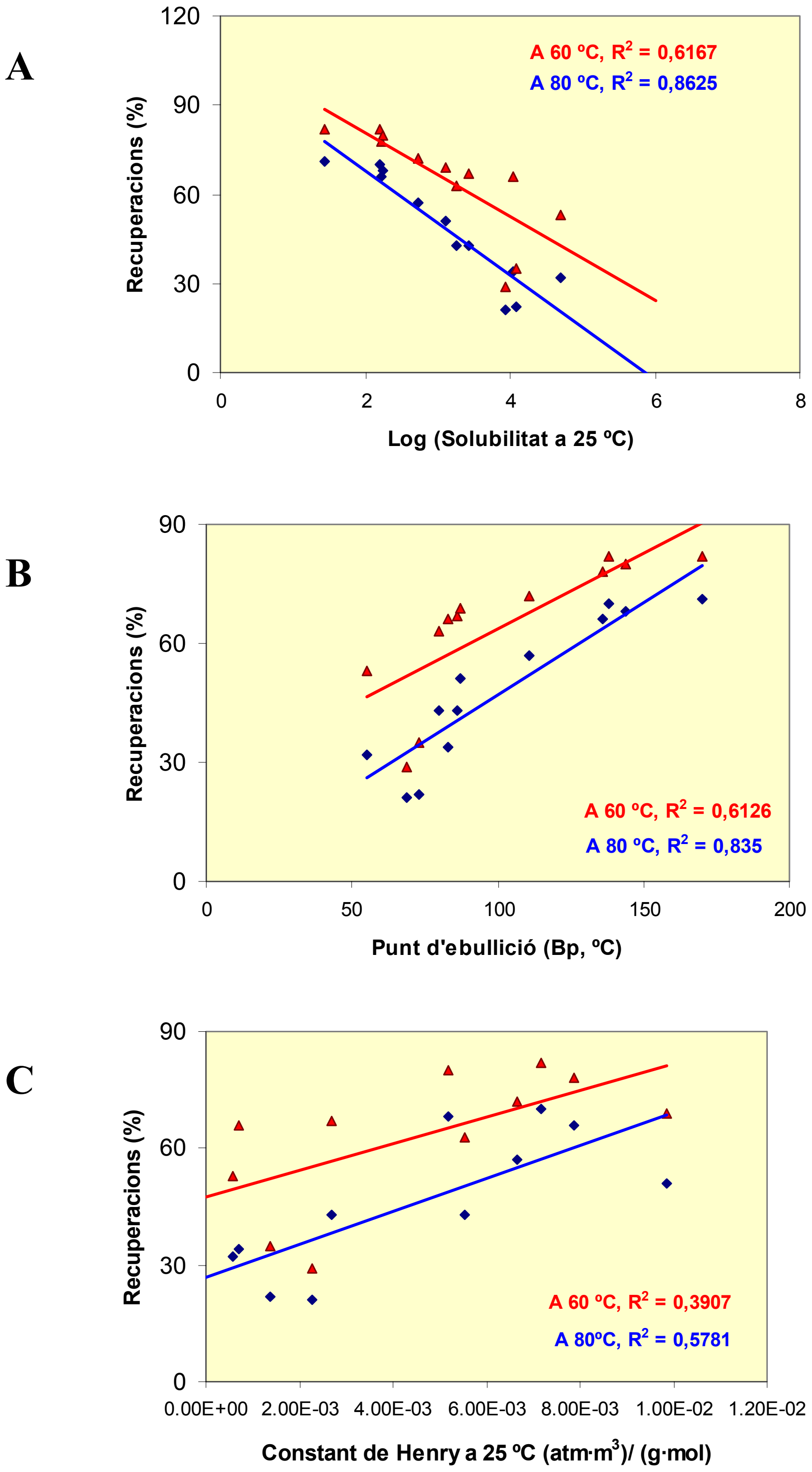

Figura 21.-Correlacions de les recuperacions relatives a 60 i 80 ºC amb les propietats físico-químiques dels analits, logaritme de la solubilitat (A), el Bp (B) i la Hc (C).

La utilització del mostrejador *Terra Core* (*Figura 22*) d'un sol ús s'ha provat com útil, senzill i força reproduïble (5,1 ± 0,7 g, el que representa una desviació estàndard relativa del 14%) a la campanya de presa de mostres pel projecte europeu PROMOTE, que es va realitzar a Polònia a finals de maig de 2006.

Figura 22.-Presa de mostres de sòl amb el mostrejador Terra Core.