DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN SOIL BY PURGE AND TRAP HRGC/ITMS

Romero-Lacal, Jorge[1].
(1) AGBAR-Aigües de Barcelona. Pg. Sant Joan 39, 08009-Barcelona (Spain).

Introduction:

Monitoring of volatile organic compounds in the environment has become a subject of concern due to the fact that many of these compounds are toxic and persistent. Several chemical types of volatile organic compounds (VOCs) have been detected in environmental water and wastewater from industrial dumping. This contamination is directly related to the contamination observed in soils and mud. Solvents, from different types of industrial uses or from domestic uses, are the most important group of contaminants. The Spanish regulations RS-9/2005 of 14 January and RD-10/1998 of 21 April establish the physicochemical quality for the classification and subsequent processing of contaminated soil and waste according to concentration levels for several organic compounds, among which we can find many solvents and other VOCs.

This work shows sample preparation and extraction for the analysis of VOCs by the purge and trap procedure in soil samples, according to SW-846 method. Quality parameters, such as the linearity ranges, repeatability and reproducibility, efficiencies, associated uncertainty and matrix effects, are presented. The experimental work is completed with real sample results.

Experimental section:

The EPA method SW-846 for the analysis of Volatile Organic Compounds in Soil by Purge-and-Trap using Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS) is a reference method for VOCs analysis in soil and it is widely used around the world. The standard EPA SW-846 is based on EPA methods 5030, 5035 and 8260. The method is designed for use on samples containing low levels of VOCs by direct extraction or solid samples containing high concentrations of VOCs by solvent extraction with methanol as sample preparation.

Autosampler: analyses were carried out on SOLATEK-72 autosampler. 5 mL or 25 mL of water samples from 40 mL EPA-vials spiked with IS (fluorbenzene, 4bromofluorbenzene and 1,2-diclhlorobenzene d6) at 2 ppb, were sequentially transferred to P&T-teckmar after and before cleaning cycles with hot water (90ºC) of the transfer pneumatic system. Vial cup and sample needle temperatures were 30ºC and 60ºC, respectively.

Purge and Trap (P&T) analysis: analyses were carried out on a TEKMAR-3100 concentrator. Samples were purged with He (40 mL/min) into a VOCARB-3000 trap during 11 min at room temperature. A “Dry purge” of 6 min was applied before trap desorption at 250ºC during 1 min. Transfer Line, Valve oven and MCS temperatures were 150ºC, 150ºC and 310ºC, respectively.

HRGC-ITMS analysis (Instrumental Conditions): HRGC/ITMS analyses were carried out on a POLARIS/TRACE-GC 2000 (Thermo Quest, USA). Desorbed trap flow was introduced into a GC system by the SSI injector at 200ºC, Split 1/10 was applied. The analytical column was a DB-624 30 m x 320 µm x 1,8 µm film (J&W Scientific, USA). The GC temperature program was 35ºC (5 min) to 160ºC (6 min) at a rate of 6ºC/min. Helium was used as carrier gas to 42 cm/s at 30ºC. The mass spectrometer was operated in IE mode (70 eV), scanning from 35-260 uma (max. ion time of the 25 ms). GC-Transfer line and ion source temperatures were 250ºC.

Results:

Low level: the result obtained for the repeatability experiment for a selected group of VOCs (ten repetitions) was a Precision (RSD) average of 15% with a maximum of 18% for Chloroform; and accuracy (relative error) was below 10% for all VOCs except for 1,2-dichloroethane and ethylbenzene, with 23%. For ten independent experiments using MRC (reproducibility), we obtained Precision average below 10% with a maximum of 14% for 1,1,2,2-tetrachloroethane and accuracy average of 14% and 10% for two different MRC, with a maximum of 21%.

High level: six concentration levels were analyzed from 0.05 to 1000 mg/kg. The result obtained for the reproducibility experiment for a selected group of VOCs (7-10 repetitions) showed a Precision (RSD) below 12% with averages around 6% for all six concentration levels, except for 1,1,2,2-tetrachloroethane, with values slightly higher. The accuracy for reproducibility experiments was below 25% for all cases with values ranging between 5%-15% and averages around 10%. For the high level of concentration (1000 mg/kg), 30% of accuracy was obtained for xylenes due to purity of the standard mixture.

Uncertainty: the Uncertainty relative expanded (Ure) was calculated from reproducibility results using “black box method” according to Eurachem Guide. The obtained result ranged between 11%-29% and 10%-30% for low level and high level methods, respectively.

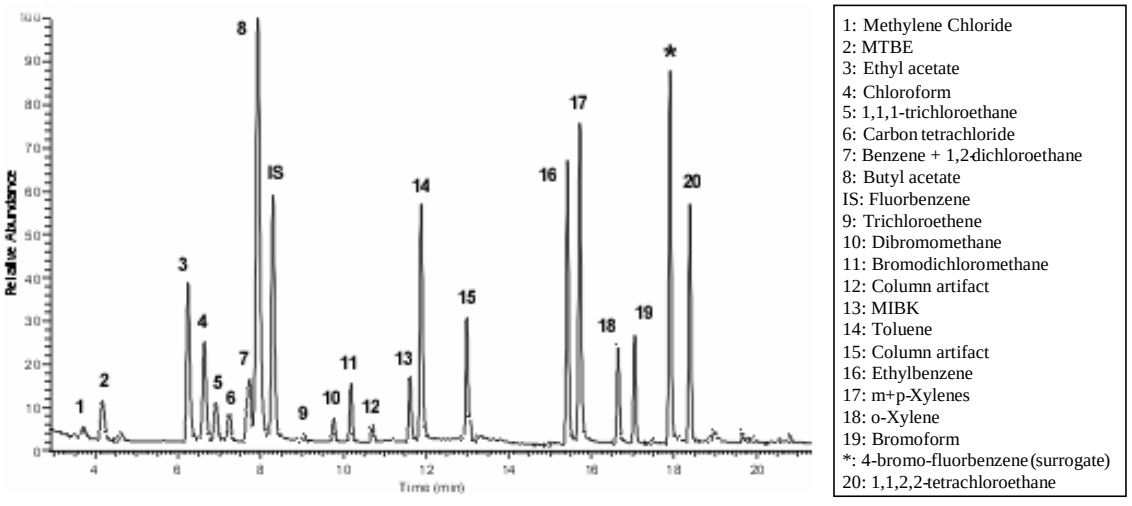

Figure 1: High level VOCs analysis by PT/GC-IT. MRC, 0.5-5 mg/kg for each compound.