Soil Gas Monitoring - The Current State of the Art

Soil gas investigations have become a key tool in evaluating the extent of Volatile Organic Compounds (VOCs) contamination in soil and groundwater. This is used to ascertain the extent of contamination as well as to evaluate the remediation progress. VOC concentration measurements also reveal subsurface migration of chemicals as pathways to indoor air vapor intrusion.

Soil gas is collected using sampling probes of various lengths to extract vapors at specific depths using evacuated canisters as a means to collect the sample without the need for sampling pumps. Contamination is pinpointed without using time consuming drilling operations, effectively determining the concentrations of contaminants with minimal disturbance to the surrounding environment. It is important to collect the vapour sample at controlled flow rates and with small sample volumes so that the sampling is not compromised by nearby points of contamination. The analysis of the vapor sample is performed using EPA method TO-15, which is an air monitoring method utilising a multi-staged, cold trapping system that can separate the major air components, nitrogen, oxygen, carbon dioxide, and water from the target VOCs of interest prior to injection into a gas chromatograph/mass spectrometer (GC/MS).

In order to monitor filling of an evacuated canister at a specific fill rate, a sampling train such as that shown in figure 1 is used. This device has a critical orifice that controls the flow rate to just under 200 mL/min. and has a vacuum gauge in line so that a visual assessment can be made during the filling process. Canisters feature a fused silica lining, called Silonite, that provides an extremely inert receiving vessel to collect soil vapour. Samples held within the Silonite coated canisters have a proven stability of many weeks. Once sampling is complete, canisters are sent to a laboratory for analysis by TO-15.

Advancements in laboratory instrumentation, combined with years of R&D, have resulted in the development of a new vapour pre-concentrator, the model 7150 from Entech Instruments, Inc., which is ideally suited for soil gas analysis. The 7150 uses a first stage "Active SPME" trap to recover compounds boiling from C_{11} and higher, while a second and third stage trap perform water elimination and VOC preconcentration, respectively. Water is eliminated using a direct vapour to solid dehydration process, allowing the recovery of compounds as light as ethane or as polar as methanol without losses. The third stage uses Tenax cooled to -40°C to allow all compounds listed in EPA Methods TO-14A and TO-15 to be recovered quantitatively, including reactive sulphur compounds. Rather than using liquid nitrogen, much less expensive liquid carbon dioxide is used to cool each of the 3 trapping stages. The initial thick film column acts to dynamically refocus the sample desorbed from the Tenax trap in order to provide a much faster injection rate onto the GC column. Liquid carbon dioxide is more amenable cryogen for mobile laboratory use, will not vent over time and can be run long distances using standard ¼ inch tubing without the need to insulate the delivery lines.

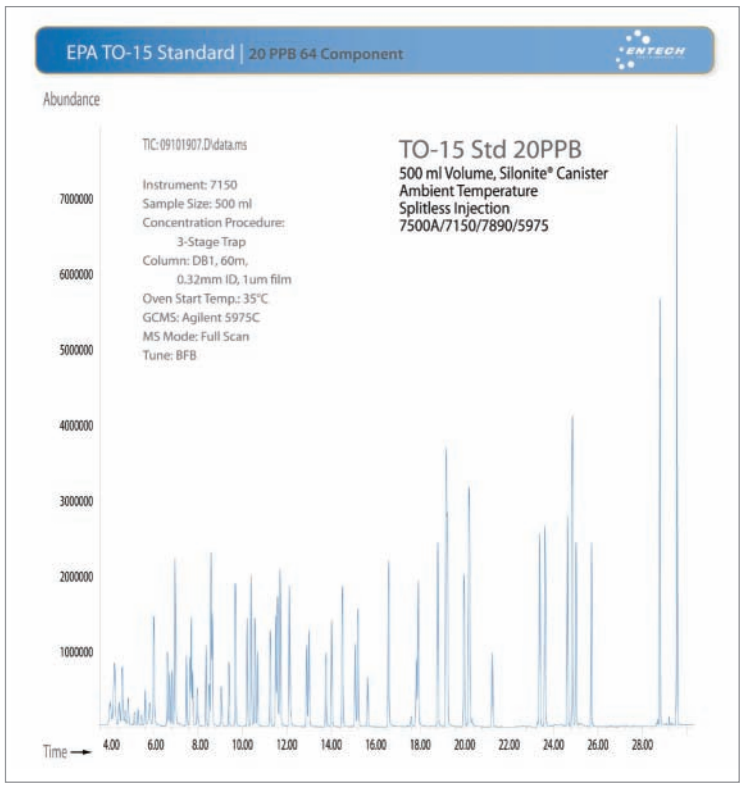

Figure 2: Chromatogram of EPA TO-15 standard showing a wide polarity range of compounds ranging in volatility from C_2 to C_{13}

Figure 2 shows a 20µg/L, EPA TO-15 standard. In this example a 500 mL aliquot was taken from a 6 litre Silonite deactivated canister at ambient temperature, concentrated and transferred to the GC column under splitless conditions. The instrumentation used was an Entech 7150A Headspace Pre-concentrator mounted on an Agilent 7890-5975C GC-MSD.

The Entech 7150 uses a unique volume measurement approach directly measuring the volume of sample that has passed through the 3-stage trapping system, rather than time integrating the flow from a mass flow controller. Start-up fluctuation and transient flows common with mass flow controller based pre-concentration systems are eliminated, as are the large internal volumes found in most mass flow controllers that make smaller sample volume measurements difficult.

As soil gas measurements are in the range of 2 µg/L to 10 µg/L, an ideal sample volume is 20 mL splitless, or 100 mL when splitting 5:1. Obtaining quantitative results for such a large concentration range can often require 2 analyses, one on the original sample to report from 2 to 200 µg/L and a second on the diluted sample (as needed) to measure compounds from 200 to 10,000 µg/L. The dilution of samples using Silonite Minicans is simple to perform, as a 16 gauge syringe can be inserted directly into the Micro QT valve to extract a known volume of sample for delivery into a dilution canister or deactivated glass Bottle-Vac sampler.

As per the requirements of EPA Method TO-15, canisters must be cleaned and evacuated prior to use. Canisters can be cleaned in a single batch, and then certified as clean by simply filling and analysing one canister out of every batch.. In general, the more inert the canister, the more effective this approach becomes as carry-over after the cleaning process is reduced. If individual canisters have adsorptive or absorptive surfaces internally, then the level of contamination remaining may not be reflected in the analysis of an "inert" canister from that

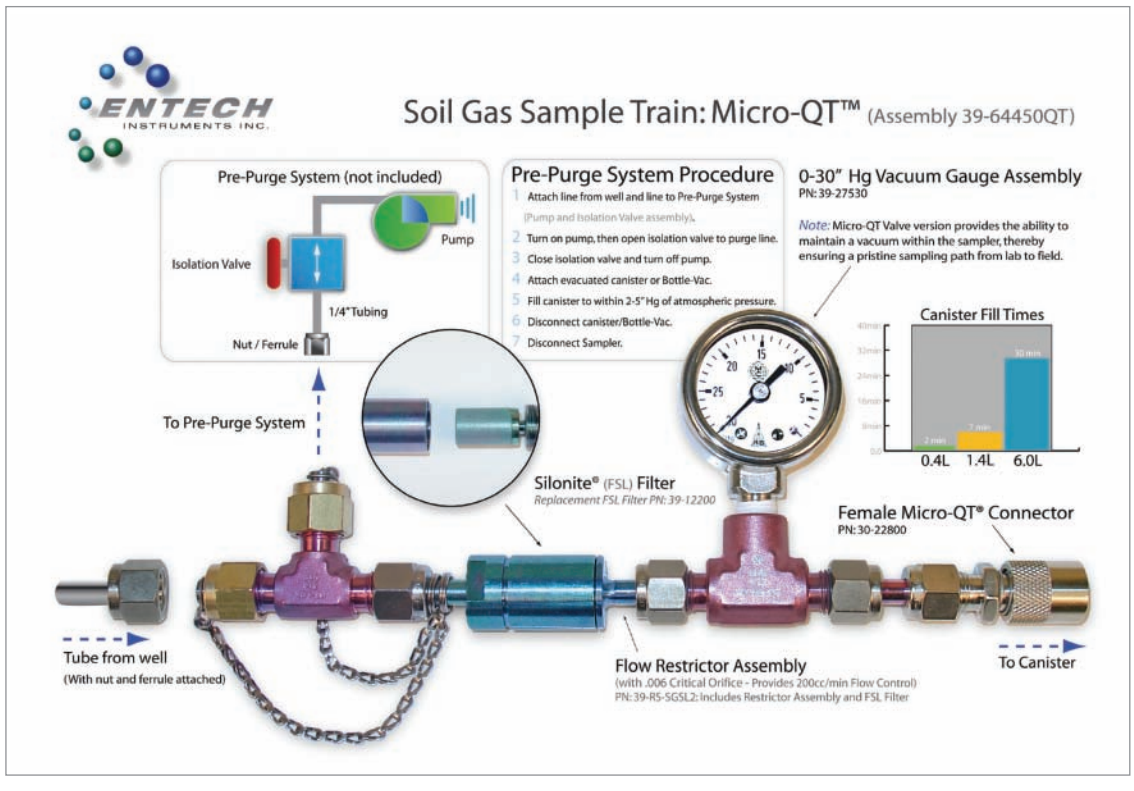

Figure 1: Passivated Soil Gas Sample Train incorporating a 200 mL/min critical orifice for precise control of the sample flow.

Internal Standards	13. Isopropyl Alcohol	33. Cyclohexane	55. Styrene
1. Bromochloromethane	14. 1,1 – Dichloroethene	35. 2,2,4–Trimethylpentane	56. o–Xylene
34. 1,4 – Difluorobenzene	15. Trichlorotrifluoroethane	36. Heptane	57. Bromoform
50. Chlorobenzene–d5	16. Allyl Chloride	37. Trichloroethene	58. 1,1,2,2–Tetrachloroethane
	17. Methylene Chloride	38. 1,2–Dichloropropane	60. 4–Ethyltoluene
System Monitoring Compounds	18. Carbon Disulfide	39. 1,4–Dioxane	61. 1,3,5–Trimethylbenzene
59. 4 – Bromofluorobenzene	19. trans – 1,2 – Dichloroethene	40. Bromodichloromethane	62. 1,2,4–Trimethylbenzene
	20. Methyl tert – Butyl Ether	41. cis–1,3–Dichloropropene	63. 1,3–Dichlorobenzene
Target Compounds	21. Vinyl Acetate	42. 4–Methyl–2–pentanone	64. Benzyl Chloride
2. Propene	22. 1,1–Dichloroethane	43. trans–1,3–Dichloropropene	65. 1,4–Dichlorobenzene
3. Dichlorodifluoromethane	23. 2–Butanone	44. Toluene	66. 1,2–Dichlorobenzene
4. Chloromethane	24. Hexane	45. 1,1,2–Trichloroethane	67. 1,2,4–Trichlorobenzene
5. Dichlorotetrafluoroethane	25. cis–1,2–Dichloroethene	46. 2–Hexanone	68. Hexachlorobutadiene
6. Vinyl Chloride	26. Ethyl Acetate	47. Dibromochloromethane	
7. 1,3 – Butadiene	27. Chloroform	48. Tetrachloroethene	
8. Bromomethane	28. Tetrahydrofuran	49. 1,2–Dibromoethane	
9. Chloroethane	29. 1,1,1–Trichloroethane	51. Chlorobenzene	
10. Bromoethene	30. 1,2–Dichloroethane	52. Ethylbenzene	
11. Trichlorofluoromethane	31. Benzene	53. m–Xylene	
12. Acetone	32. Carbon Tetrachloride	54. p–Xylene	

Table 1. The compounds contained in the EPA TO-15 standard mixture used to generate the chromatogram above.

batch. In general, certification of recovery after the manufacturing process is critical in determining whether a canister has been individually tested for inertness, as imperfections during the manufacturing process that are not identified prior to shipping can be the greatest cause of poor performance with the canister technique.

Since soil gas can vary in concentration by 4 orders of magnitude, it is important to treat the entire sample train as part of the canister and subject it to the same cleaning procedure as the canister itself. Having the ability to seal the sample train prior to shipping to the field, or pressurising the system to validate its isolation until the point of sampling, can improve the certainty in the data collected.

Soil gas analysis is a technique that is becoming increasingly popular as a means of evaluating the extent of contamination in soil and groundwater. It is now a mature approach, with all of the required elements in place to produce good quality data in a reliable fashion.

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Fast, Precise Elemental Analysis for Process Control

The iQ II EDXRF Spectrometer gives precise, accurate analytical results on demanding process control samples, says manufacturer **Spectro Analytical Instruments GmbH** (Germany). Oil refiners, lubricating oil manufacturers, mineral and cement producers and many other industries will find this instrument attractive because of its simplicity of operation and impressive sensitivity for the often critical "light" elements like Na, Mg, Al, Si, P, S and Cl.

The advanced polarised X-ray optical system uses a curved HOPG (highly oriented pyrolytic graphite) crystal located very close to the sample, ensuring optimum excitation for light elements. By combining this optical system with a 50 kV X-ray tube and an exceptionally powerful Peltier-cooled Silicon Drift Detector, performance approaching that of much more expensive Wavelength Dispersive (WDXRF) instruments can be achieved in many applications, for both light and trace elements in liquid and loose powder samples, Helium flushing can be used with the iQ II to enhance light element performance, but unlike most small EDXRF instruments the user can also measure pelletised or fused samples under vacuum conditions, thereby dramatically reducing operating costs over the life of the instrument. A new generation of sample cassettes makes possible the extremely accurate sample positioning system in the iQ II, helping to achieve the high analytical precision required for industrial QC applications.

A selection of ready-to-go applications software packages is available for important applications such as ultra-low Sulphur in fuel oil, lubricating oil additives, cement and slag analysis. Where appropriate, these methods comply with international norms.

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New Brochure for On-Site Oil/Grease Measurements in Water and Soil

The InfraCal TOG/TPH Analysers for oil/grease concentration levels are highlighted in a new brochure published by **Wilks Enterprise** (USA). These analysers are specifically designed for easy, on-site infrared measurement of total oil and grease (TOG), total petroleum hydrocarbon (TPH), and fat, oil and grease (FOG) concentration levels in water and soil samples. The InfraCal TOG/TPH Analysers are used worldwide for analysing produced water on off-shore platforms or wastewater in refineries, industrial plants or treatment facilities and soil studies at remediation sites or around underground storage tanks. Typical analysis time is under 15 minutes, including extraction process.

The InfraCal TOG/TPH Analysers have been used by the Water Environment Research Foundation (WERF) to evaluate performance of grease interceptors and their effect on wastewater, by the ASTM to develop Method D 7066-04, and by numerous companies to meet new European discharge regulations. InfraCal TOG/TPH models are available for use with a wide variety of extracting solvents such as hexane, pentane, Vertrel MCA, Freon, hydrocarbon-free grade of perchloroethylene, S-316 or AK-225.

All InfraCal analysers are portable (operable from a 12 volt dc power supply) and weigh less than 5 lbs. Pushbutton, user-friendly operation makes them easy to use with minimal training. The analysers can read out in infrared absorption values or they can be calibrated to display concentrations directly in any desired format such as ppm or milligram/kg. A wide range of accessories, such as printer and carrying case increase the versatility and capabilities of the Infracal TOG/TPH Analyser.

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