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Comparison of data quality produced by an on-site field GC/MS and an off-site permanent laboratory GC/MS: support of a cleanup action at an inactive drum recycling facility☆

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Abstract

Remediation activities require reliable analytical data when removal and treatment operations are being performed. Traditionally, quality information was only available from established laboratories at off-site locations. Although the assay results were accurate and precise, turnaround time was not prompt. The delay of these results has resulted in the site work not being as efficient or effective as could be.

Recently, great strides have been made in field analytical equipment, which has been designed to provide data of similar quality as permanent laboratories. To examine this point, samples were collected at a site undergoing remediation for analysis both on site and at a permanent laboratory. The data generated from a field transportable gas chromatograph/mass spectrometer (GC/MS) was compared to that produced by a GC/MS stationed in a fixed laboratory. The field transportable GC/MS was established on site and analyzed air samples collected on charcoal adsorbent tubes. Additional collocated air samples were collected for analysis by a GC/MS located in a permanent laboratory.

Keywords: Gas chromatography/mass spectrometry; Field analytical instrumentation; Drum recycling facility; Cleanup action

1. Introduction

Remediation activities at hazardous waste sites are often directed by the US Environmental Protection Agency (US EPA). Additionally, the Environmental

☆ Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

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Response Team (ERT) of the US EPA functions as a national response team to be utilized by the US EPA, as well as other federal, state, and local agencies whenever they encountered particularly dangerous or technologically complex situations. Based on the threat posed by unsecured hazardous substances at a former drum recycling operation, the US EPA conducted a cleanup action under the authority of the Comprehensive Environmental Resource Compensation and Liability Act (CERCLA). During removal activities the US EPA/ERT was requested to provide a variety of air monitoring, sampling and on-site analytical capabilities to ensure on-site activities were being performed in a manner that was safe for workers and adjacent residences.

The site history showed that drum recycling occurred at the 8-acre site for more than 20 years. The drums contained a wide variety of hazardous wastes, including, oils, acids, solvents, paint wastes, polychlorinated biphenyls (PBCs), pesticides, and radioactive material. The previous operating practice had been to dump the residual drum contents into a floor drain leading to a buried discharge line or onto the ground directly. The drums were then passed through an incinerator to remove any further residue and later refurbished. A bead blaster utilizing lead pellets to remove drum paint was also used.

The facility was in a state of disarray with drum piles, crushed automobiles, and scrap metal scattered throughout the site. Several phases of remediation effort conducted at the site included drum removal, soil excavation and solidification activities. Due to the types of remediation activities and the proximity of the adjacent neighborhood, the air pathway was of concern and the analytical data from the air monitoring and sampling was a means to address this concern and help direct remediation activities.

The air data generated from this site work examines the results from (1) the on-site laboratory using a modified US EPA Toxic Organic (TO) methods TO1 and TO2 and (2) the results from the permanent laboratory equipment using a modified National Institute for Occupational Safety and Health (NIOSH) methods 1500, 1501, and 1003. The data sets produced by the field analytical instrumentation and the permanent laboratory instrumentation are different in many respects, one being that each method specifies a given target compound list. The compounds which are congruent between both sets are: 1,1,1-trichloroethane, carbon tetrachloride, benzene, trichloroethene, toluene, ethylbenzene, xylene (total), styrene, and 1,1,2,2-tetrachloroethane. These compounds will be reviewed for similarities in the field and the permanent laboratory analytical results.

2. Sample collection

2.1. On-site laboratory

Sorbent tubes with 625-milligram (mg) of charcoal sorbent were utilized to sample for volatile organic compounds (VOCs) following a modified Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

methods: TO1, Method for the Determination of Volatile Organic Compounds in Ambient Air Using TENAX Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS) and TO2, Method for the Determination of Volatile Organic Compounds in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS) [1]. The sampling train consisted of a low flow personal sampling pump connected to the sorbent tube. The sampling pump was calibrated using a flow meter to pull approximately 50 to 100 ml/min of air through the sorbent tube. Sampling time varied depending on site activity, but ranged from approximately 250 to 500 min, resulting in sample volumes ranging from 17 to 45 l. At the end of the sampling period samples were packaged, Chain of Custodies written, and the samples were given to the chemist on site for GC/MS analysis.

2.2. US EPA/ERT Edison, NJ laboratory

Sampling of VOCs utilizing charcoal sorbent tubes was conducted following modified NIOSH methods: Method 1500 Hydrocarbons, BP 36–126 °C; Method 1501 Hydrocarbons, Aromatics; and Method 1003 Hydrocarbons, Halogenated [2]. The sampling train consisted of a 600 mg charcoal sorbent tube connected to a low/high flow personal sampling pump. The sampling pump was calibrated using a flow meter to pull approximately 1 l/min of air through the sorbent tube. Sampling durations were consistent with the previously stated times with final volumes of 250 to 500 l. At the end of the sampling period samples were packaged, Chain of Custodies written, and the samples shipped to the US EPA/ERT laboratory in Edison, NJ for GC/MS analysis by the Response Engineering and Analytical Contract (REAC).

3. Instrumentation

3.1. On-site laboratory

The field analysis used a Viking GC/MS, which is a transportable, multicomponent system consisting of a GC, MS, and data system [3] . The MS is based on the Hewlett-Packard Model 5971A Mass Selective Detector. The HP 5971A uses a monolithic, fused silica mass filter with four electrically conductive hyperbolic surfaces. The analyzer can scan the mass range between 10 and 650 atomic mass units (amu) at eight selectable scanning speeds up to 2000 amu per second with 0.1 amu resolution. The GC is able to house a variety of capillary columns with internal diameters of 0.30 millimeters (mm) or smaller and up to 105 m long. It has the capability of heating the oven at a single programmable ramping rate of up to 20 °C per minute. It may be operated in the split or splitless mode and has a cryofocusing mode that allows the trapping of light volatiles at the head of the column to improve chromatography.

3.2. US EPA/ERT Edison, NJ laboratory

The US EPA/ERT Edison, NJ laboratory analysis used an Hewlett-Packard 5890A GC equipped with an Hewlett-Packard 5970 Mass Selective Detector [4], a 7673A autosampler and controlled by an Hewlett-Packard RTE-6/VM computer.

4. Instrument operational parameters and analytical procedure

4.1. On-site laboratory

The instrument conditions were:

Desorber conditions:

Desorb temperature	240 °C,
Desorb time	2.0 min (CMS only)
Cryotrap temperature	− 70 °C.

Chromatographic conditions:

GC column	0.32 mm × 60 m Restek RT_x-Volatiles
Initial temperature	25.0 °C
Initial hold time	0.5 min
Ramp rate	8.0 °C/min
Final temperature	230.0 °C
Run time	25.5 min
Split ratio	30:1
Mass scan range	35 to 250 amu

Tuning and GC/MS calibration was performed at the beginning of each day to verify that acceptable performance criteria could be achieved. The mass spectrometer was first automatically or manually tuned on perfluorotributylamine (PFTBA). PFTBA tuning was done to demonstrate that the instrument was operating properly. After PFTBA tuning, *p*-bromofluorobenzene (BFB) was analyzed to check the GC column performance and as a GC/MS performance standard.

This performance test passed the criteria set forth in US EPA Method 624 before any samples, standards, or blanks were analyzed, and was repeated every 12 h of continuous operation. If the criteria were not met, the instrument was re-tuned and the BFB standard was re-injected.

Before any analysis, the GC/MS was initially calibrated using standards contained in pressurized cylinders at approximately 1 part per million by volume (ppmv) in nitrogen. A single-point calibration was created by injecting a 50 ml volume of the 1 ppmv gas standard onto the thermal desorber and analyzing it in the GC/MS. For each compound in the calibration, the retention times and relative abundances of selected ions are stored on the hard disk of the GC/MS computer to be used for compound identification.

All samples were prepared for GC/MS analysis by using a thermal desorption/cryogenic trapping unit. The unit was equipped with a 6 mm × 115 mm oven chamber for desorbing samples and a cryogenic trap consisting of a tube cooled by liquid carbon dioxide at the head of the pre-column. The pre-column was installed to prevent the column from being exposed to the wide temperature range that occurs at the trap. After sample and internal standards were introduced on a Supelco™ Carbotrap 300 (CMS) 625-mg charcoal thermal desorption tube, they were thermally desorbed by heating the oven while purging with helium.

All CMS samples were handled with cotton cloth or gloves and tweezers to avoid contamination. Analysis of a cartridge sample followed the procedures specified below:

1. Place the cartridge in the desorption oven with the side with the largest mesh CMS in first. Engage the load cycle.
2. During the load step, a 20 parts per billion by volume (ppbv) mixture of the internal standards bromochloromethane (BCM) and BFB are spiked onto samples by injecting 10 ml into the sample stream.
3. After the internal standards have been introduced into the tube and the dry purge cycle has been completed, the cryogenic trap is cooled to − 70 °C with liquid carbon dioxide.
4. Once the cryotrap has been cooled, the thermal desorber is automatically stepped to the desorb cycle, allowing the internal standards to desorb from the CMS with the sample.
5. After the transfer is complete, the sample is injected by heating of the cold trap in the GC oven to 25 °C. The analysis then follows the chromatographic conditions.

4.2. US EPA/ERT Edison, NJ laboratory samples

The instrument conditions were:

Column	Restek RTx-5 (crossbonded SE-54) 30 m × 0.25 mm ID, 0.50 μm film thickness
Injection temperature	260 °C
Transfer temperature	260 °C
Source temperature	220 °C
Temperature	30 °C for 4 min 4 °C/min to 150 °C 8 °C/min to 195 °C hold for 1 min
Splitless injection	split time = 45 s
Injection volume	1 μl.

The GC/MS was calibrated using 6 NIOSH volatile standards at 1, 2, 10, 25, 50, and 100 microgram per milliliter (μg/ml) solutions. Criteria have not been established for the System Performance Check Compounds, (SPCC), however, a Contract Lab Program (CLP) criterion of less than 30% Relative Standard Deviation (RSD) for all analytes is being tentatively adopted. Before analysis each day the system was tuned

to decafluorotriphenyl phosphine (DFTPP) and had to pass a continuing calibration check by analyzing a 25 μg/ml daily standard in which the response factors for all compounds are compared to the average response factors of the 6-point calibration curve. All compounds should have a difference of less than 25%. Sample quantification was based on the response factor of the daily 25 μg/ml standard mixture.

Carbon tubes were extracted by removing the front and back portions of a two stage carbon tube and extracting each portion separately with carbon disulfide. The procedure which outlines the sample extraction is listed below:

1. Remove foam plug from the back portion of the tube and discard.
2. Remove the carbon packing from the back of the tube and place it in a 3.7 ml screw top sample vial. Name this vial "back" along with the sample number.
3. Remove the foam supporting the carbon in the front portion of the tube and discard it.
4. Place the carbon packing in a second sample vial and label it "front".
5. Pipette 2.0 ml of "benzene free" or clean carbon disulfide in the vials with the carbon packing, and screw the tops on tightly.
6. Place the sample vials (carbon and CS_2) in a sonic bath for 10 to 15 min.
7. When done sonication, let settle for 30 min, then transfer 1.0 ml of CS_2 from the vial containing the carbon and CS_2 to a 1.0 ml autosampler vial.
8. Add the internal standards mix.

The samples are now ready for GC/MS analysis by placing in the autosampler and having 1 μl injected through the septum.

5. Results

5.1. On-site laboratory

Analytes were identified and quantitated by the Hewlett-Packard Chemstation software. This software uses reconstructed, extracted ion chromatograms matched with retention time windows to identify and quantitate target compounds. The Chemstation software allows the analyst to validate the mass spectra and adjust quantitation manually when necessary. The quantitation results list the retention time, the scan number, the peak area, and the concentration in ppbv for each target compound and internal standard. The target compound results were calculated in ppbv using the following equation:

$$\text{Concentration (ppbv)} = \frac{\text{Concentration (nl)} \times 1000}{\text{Undiluted sample volume (ml)}}.$$

A summary of the GC/MS target compound results are listed in Table 1. Results are given in ppbv for all samples.

5.2. US EPA/ERT Edison, NJ laboratory samples

Analytes were identified and quantitated by the Hewlett-Packard Aquarius software. This software uses reconstructed, extracted ion chromatograms matched with

Table 1
On-site GC/MS and US EPA/ERT Edison, NJ off-site laboratory GC/MS results (concentrations in ppbv)

Date	9/14/93	9/14/93	9/14/93	9/14/93
Location	Location 8	Location 8	Location 9	Location 9
Analysis	Off-site	On-site	Off-site	On-site
Compound				
1,1,1-Trichloroethane	1.6	0.2	1.9	1.9
Trichloroethene	ND[a]	ND	ND	1.1
Tetrachloroethene	2.3	4.0	4.4	12
Benzene	ND	0.5	2.6	2.7
Toluene	1.6	2.3	2.6	5.0
Xylenes (total)	0.6	1.5	0.6	2.0
Styrene	4.4	6.7	ND	1.0
Date	9/15/93	9/15/93	9/15/93	9/15/93
Location	Location 8	Location 8	Location 9	Location 9
Analysis	Off-site	On-site	Off-site	On-site
Compound				
1,1,1-Trichloroethane	ND	ND	ND	ND
Trichloroethene	1.8	3.2	ND	1.4
Tetrachloroethene	3.4	8.7	0.9	1.8
Benzene	ND	1.5	3.6	4.0
Toluene	2.5	4.3	6.2	6.2
Xylenes (total)	1.7	5.0	1.3	2.8
Styrene	4.3	7.4	2.0	3.4
Date	9/16/93	9/16/93	9/16/93	9/16/93
Location	Location 8	Location 8	Location 7	Location 7
Analysis	Off-site	On-site	Off-site	On-site
Compound				
1,1,1-Trichloroethane	71	20	3.1	ND[a]
Trichloroethene	30	43	1.0	3.9
Tetrachloroethene	9.0	19	ND	2.0
Benzene	2.5	2.8	ND	0.6
Toluene	5.2	9.7	ND	1.9
Xylenes (total)	3.5	7.5	0.3	1.3
Styrene	ND	2.0	ND	0.3

[a] Not detected.

retention time windows to identify and quantitate target compounds. The Aquarius software allows the analyst to validate the mass spectra and adjust quantitation manually when necessary. The quantitation results list the retention time, the scan number, the peak area, and the concentration in ppbv for each target compound and internal standard. The following equations were used to calculate the analyte in total micrograms per sample:

$$\mu g/\text{sample} = C_u \times V \times \text{DE} = \frac{A_u \times C_{is} \times V \times \text{DE}}{A_{is} \times \text{RF}}$$

where C_u is the concentration of the analyte (μg/ml), V is the extraction volume (ml), DE is the desorption efficiency = (% Recovery)/100, A_u is the area of the analyte, C_{is} is the concentration of the internal standard (μg/ml), A_{is} is the area of the internal standard and RF is the response factor.

The concentration of the analyte in mg/m^3 and ppbv (parts per billion by volume) is calculated using the following:

$$ppb = \frac{mg/m^3 \times 24.45 \times 1000}{MW},$$

where MW is the molecular weight of the analyte.

A summary of the GC/MS target compound results are listed in Table 1. Results are given in ppbv for all samples.

6. Conclusions

The sample collection and analysis by the on-site laboratory was conducted by using 625 mg charcoal sorbent tubes sampled at a flow rate of 50–100 ml/min, thermally desorbed into the GC/MS and analyzed by modified US EPA TO1 and TO2 methods. The sample collection and analyses by the US EPA/ERT laboratory were conducted by using 600 mg charcoal sorbent tubes sampled at a flow rate of 1 l/min, extracted with CS_2, liquid injected into the GC/MS and analyzed by modified NIOSH 1500, 1501, and 1003 methods. The data sets produced by the two analytical instruments following different methods showed good agreement for similar target compounds. Given the fact that the US EPA/ERT laboratory performed a 6-point calibration curve and employed extraction efficiency data, and the on-site laboratory data was produced using a 1-point calibration curve and no desorption efficiency data, the similarity of the data sets is encouraging. The significance of these results are (1) on-site analysis can provide data of high quality, (2) on-site analysis can supply results more rapidly than off-site laboratories, and (3) remediation efforts can be directed more effectively using accurate and timely information.

Although further testing is needed to examine additional compounds, the on-site laboratory demonstrated that it could produce reliable data of high quality. Furthermore, the on-site laboratory showed that for some compounds, which can be thermally desorbed, this sample introduction system for the GC/MS has significant advantages over sample introduction systems which require sample preparation by extraction. Not only are the time considerations associated with the extraction step eliminated, solvent use is avoided.

References

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