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VOLATILE ORGANIC COMPOUND MONITORING BY PHOTO
ACOUSTIC RADIOMETRY

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Volatile Organic Compound Monitoring by Photoacoustic Radiometry

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ABSTRACT

Two methods for sampling and analyzing volatile organics in subsurface pore gas were developed for use at the Hazardous Waste Disposal Site at Los Alamos National Laboratory. One is Thermal Desorption Gas Chromatography Mass Spectrometry (TDGCMS), the other is Photoacoustic Radiometry (PAR). Presented here are two years worth of experience and lessons learned as both techniques matured. The sampling technique is equally as important as the analysis method. PAR is a nondispersive infrared technique utilizing band pass filters in the region from 1 to 15 μm . A commercial instrument, the Model 1302 Multigas Analyzer, made by Bruel and Kjaer, was adapted for field use. To use the PAR there must be some *a priori* knowledge of the constellation of analytes to be measured. The TDGCMS method is sensitive to 50 analytes. Hence TDGCMS is used in an initial survey of the site to determine what compounds are present and at what concentration. Once the major constituents of the soil-gas vapor plume are known the PAR can be configured to monitor for the five analytes of most interest. The PAR can analyse a sample in minutes, while in the field. The PAR is also quite precise in controlled situations.

INTRODUCTION

At the Los Alamos National Laboratory Hazardous Waste Disposal Site volatile organic compounds are monitored in soil pore gas by sampling a network of 35 wells explicitly drilled for this purpose. Monitoring began in 1983 using sorption techniques for sampling and Gas Chromatography/Mass Spectrometry GCMS for analysis. The initial GCMS method used activated coconut charcoal to capture the chemical compounds. Extraction of the sorbed material was done with carbon disulfide. The analysis was sensitive to 13 analytes. There was significant scatter in the data. In 1993 a new sampling technique was adopted for sorption and a thermal desorption method TDGCMS was adopted for analysis. The sample collection device uses a three element collection tube with carbo-sieve and carbo-trap, and a split flow to increase the range of concentrations over which measurements are made. The sampled volume is measured using an integrating mass flow meter. PAR was introduced in conjunction with the TDGCMS method. In this presentation an assessment of the utility of each method is given. A commercial PAR instrument, intended for indoor air quality monitoring, was adapted for field use. The PAR gives quick results with good precision and accuracy once the constellation of analytes is known. The machine is configured to measure the 5 most prevalent compounds.

A distinction should be made from the outset about what "the plume" is. There is an agglomeration of several distinct plumes. The plume is in the ground and results from the dispersion of various substances thru the soil after deposition. The dispersal rate for more volatile compounds will be higher than for less volatile compounds. The rate also depends upon the medium in which the disposal takes place. The ground in effect will act as a gigantic chromatograph. The constellation of analytes disposed in the older pits and shafts is different from the newer ones. In the older shafts are the more hazardous materials such as benzene and carbon tetrachloride. As safer materials became available they were used in preference to the older more dangerous materials. Hence in the newer disposal sites are found tetrachloroethene (also known as perchloroethylene (PCE) or perc, common dry cleaning fluid), trichloroethene (TCE), and 1,1,1-trichloroethane (TCA). The most hazardous of these three substances is perc, next is TCE because of its action on the central nervous system and its narcotic effect. The safest is TCA. In the newest sites Freons® are found. These are chlorofluorocarbons CFCs which are very stable and rather inert; hence they pose less biological hazard. However, since the Montreal Protocol of 1987, CFCs have been proscribed in an effort to "save the ozone."

According to EPA regulations and federal law (40 CFR part 261) only methods explicitly mentioned in SW846, Test Methods for Evaluating Solid Waste¹ maybe used in site characterization involving hazardous waste defined in section 3001 Resource Conservation and Recovery Act RCRA (PL

94-580). For halogenated volatile organics Method 8000: Gas Chromatography², Method 8010: Halogenated Volatile Organics,³ Method 8240: Chromatography/Mass Spectrometry for Volatile Organics⁴ are required in analysis. The sampling must be done in accordance with Method 0030: Volatile Organic Sampling Train.⁵ The Analytical Procedure must be in accord with Method 5040: Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train.⁶ Though these documents detail exact procedures, in fact they are, in our application, inadequate. Prior to 1993 the sampling and analysis was done by the book, as specified above. More than 25,000 samples were taken to monitor the hazardous waste site from June 1988 to December 1990.

To measure the volatile organics, sorption samples were drawn from each port of each well. The purge volume was typically one "headspace," the amount of gas in the tubing leading to the sample port. The volume of gas passed thru the tube to take the sample was to be 1.2 L, the error associated with the volume being about 17%. The sorption tube contained a single sorbent, activated coconut charcoal. Desorption was by solvent extraction using carbon disulfide. Analysis was by conventional gas chromatography mass spectrometry GCMS. Thirteen analytes could be measured this way.

The scatter in the data was so great that it was unsuitable to use as a baseline for design of an extraction system. Consequently the Organic Chemistry Group devised the currently used LANL Method EO700-1 for "Thermal Desorption of Air Sampling Tubes - GC/MS," which is sensitive to 50 analytes TDGCMS. At the same time the Energy and Process Engineering Group obtained a PAR, a Bruel and Kjaer Model 1302 Multigas Analyzer. By using both the TDGCMS and the PAR methods to check each other improvements have resulted in both. The first truly high quality data from both the TDGCMS and PAR were taken during the fourth quarter of 1993.

Since that time, concentration measurements of volatile organics are made using both TDGCMS and PAR. While the TDGCMS is sensitive to 50 analytes, the PAR is best when looking for no more than 5. The PAR technique offers an advantage in the field because results are known immediately. TDGCMS analysis takes a minimum of 6 weeks.

CONCENTRATION MEASUREMENT METHODS

Development of the Thermal Desorption Method TDGCMS

To bring the TDGCMS on-line as an effective field method required some debugging. In the early stages problems were encountered with thermal degradation products appearing in the eluted vapors. There was a question whether stainless steel was catalyzing unwanted reactions in the gas path. To avoid problems of thermal degradation, the desorption temperature must be carefully controlled not to exceed 350 degrees Fahrenheit. Knowing accurately the volumes of gas passed thru the sorption tubes is critical. For the semiautomated unit, custom built for this application, the volume is inferred from an integrating mass flow meter. The unit is programmed to draw 560 mL of pore-gas, 51 mL thru one sorption tube, and 509 mL thru the other. After the sample is drawn it is set by passing an additional 170 mL of air, filtered thru a charcoal trap, thru the sorption tubes. Calibration runs, before and after field events, are important to maintain confidence in the sampling and analysis. Spiked samples are prepared by evaporation from neat compounds and from cylinders of compressed calibration gases prepared by commercial laboratories.

Drawing a sorption sample is only the beginning of the steps involved with a TDGCMS sample. There is the entire issue of Chain-of-Custody. The samples must be submitted to an organization called Sample Receiving. They in turn must give the samples to the analytical lab. While doing the sampling the samples are kept in insulated boxes with blue ice, then transferred to a holding freezer. Then they are transferred to the freezer at Sample Receiving, and finally to the freezer at the analytical lab. Because the freezer used to marshal the samples prior to submission for analysis was old, a test was run using four sorption tubes: 1. A bare sorption tube; 2. A sorption tube in its glass envelope, but with the cap removed; 3. a sorption tube in its glass envelope with the plastic cap with rubber seal on, finger tight; and 4. A control that was at room temperature away from the freezer. Freon contamination was present. In the sealed sample there was contamination at about a 1% level, with no pressure difference to draw air into the tube. The same test was run on the newer refrigerator that currently in use, with the same result. Freon contamination appears ubiquitous. To counter that problem samples are now kept in an evacuated dessicator pending submission for analysis.

Development of the PAR Method

The photoacoustic radiometer uses narrow band filters in the region where trimer or higher molecules have vibrational and rotational resonances, from 2.5 to 15 micrometers (4,000 to 650 reciprocal centimeters). Alexander Graham Bell discovered in 1880 that various airborne constituents will absorb energy from sunlight. The absorbed energy can manifest as an increase in pressure. To make the signal

more noticeable the sunlight can be chopped at an audible frequency. The Bruel and Kjaer Model 1302 Multigas Analyzer is a sophisticated embodiment of this principle.

In order to be more selective and specific in detection of particular gases, narrow band infrared filters are chosen to allow light of only specific frequencies to pass thru the sample cell. Water must always be measured and compensation must be made for its absorption anywhere in the spectrum. In addition to the filter for water five other filters may be chosen. In principle each filter may be calibrated for up to 5 different gases, for a total of 25 compounds, plus water. In practice, in the field, at most 5 gases are measured, one per filter.

The concentration range for the instrument is impressive. It will read over 10,000 times the limit of quantization. A measurement of 5 gases plus water typically takes a little over 2 minutes. Limits of quantification are typically from 0.1 ppm to 10 ppm depending upon the compound and the other constituents. Calibration of the instrument is required using the specific compounds.

Measurements of a single compound are often within 1% of the value given for the calibration gas, and the instrument will repeat to 0.5%. To put this in perspective, good GCMS data is in the 20% range. In preparation of standards by evaporation from liquids it was difficult to be certain of the mass of the liquid being injected in the test volume because evaporation rates are very high. To measure the minute amounts of analyte both micropipettes and microsyringes were tried. It helped to increase the test volume so that larger amounts of analyte were required. Larger amounts of analyte can be measured with greater confidence. Finally, a combination of a micropipette and an analytical balance was used. Our test volume was a 30 gallon drum. The drum was evacuated and the analyte injected directly into the valve used to backfill the drum. Error in standards prepared in this way are still dominated by measurements in the analyte. The evaporation rate of TCA of about 4 mg/min makes it difficult to measure 14 mg and get it into a container without significant loss. Our neat standards were within about 2%.

In a recent test two identically calibrated PARs were tested in comparison. On single spiked samples measurements by the PARs were within a few percent of each other, and within a few percent of the calibration value. However on identical gas samples from the plume measurements by the PARs could differ by as much as 20%. Which one was correct? Comparisons are being run on the same gas analyzed from sorption samples taken in the field, and from Tedlar® bag samples of gas tendered to the analysis lab where they draw samples by syringe from the bag and inject a known volume on sorption tubes to begin the TDGCMS analysis. These test results are not yet available. It is part of a pilot extraction test in process. The extraction pump was turned on 9/19/95.

Comparison

For field trials made on soil pore-gas the PAR measurements were all high relative to TDGCMS measurements, probably due to interference from similar compounds. The initial interference factors were on the order of four or five. That is, the PAR measurements would read four or five times more analyte present than TDGCMS for TCA. Depending upon which constituents are to be measured the filter choice may change. In the first quarter of '95 an effort was made to reduce the interference by looking for the most dominant compounds in the plume. The interference factor has been reduced to one to two. The PAR was used to measure 1,1,1-trichloroethane TCA, trichloroethene TCE, tetrachloroethene sometimes called perchloroethene PCE, vinyl chloride, carbon dioxide, trichlorofluoromethane or R11, and trichlorotrifluoroethane or R113. The most dominant hazardous materials are TCA, TCE, R113, R11, these are the compounds which the PAR measured since January 1995.

SAMPLING

Other Factors That Influence the Measurements

There are four different kinds of monitoring wells having 0.25 inch internal diameter tubing that connects each sampling port to the surface. The ports are generally at a depth that is a multiple of 20 feet. The newer wells are equipped with the Science Engineering Associates Membrane Instrumentation Sampling Technique (SEAMIST) membranes. The tubing attached to the sampling ports is 0.0625" internal diameter which provides at least 256 times more impedance to the passage of gases than the 0.25" tubing. The sampling depth for the newer wells is based on permeability measurements taken for each hole, and is not necessarily at multiples of 20 feet.

Sampling technique also changed as more was learned. Initially the headspace was pumped out with a large auxiliary pump and then the gas stream was switched into the PAR and the gas was pumped into the sample cell by the small internal pump of the PAR. Continuous monitoring of different wells at different depths over periods of time up to 6 hours lead us to conclude that it was best to pump at least five times the headspace volume before taking a data sample. There are numerous possible causes of transient behavior in the first part of the gas flow. After five headspaces of gas was pumped the concentration tended asymptotically to approach a value which was likely to be characteristic of the particular port.

Some very bizarre behavior has been observed for some ports. It is by no means certain that the concentration will exhibit a simple well-behaved asymptotic response to purge volume. If the lithography is complicated the pumping curve is likely to be complicated. For the wells measured in this study a five-head-space rule-of-thumb seems to work adequately. Because some wells are intrinsically dirty a lot of pulverized soil and dust and sand is entrained and must be filtered out before it gets into the equipment. Hence gas impedance is not solely a function of the tube diameter and length.

When more than 40 Torr back pressure develops in the course of filling the PAR sample cell the measurement is compromised. With the small diameter tubing the back pressure is always greater than 40 Torr, so a different technique must be used for the newer wells. The tubing ID for the older wells is 0.25", for the newer wells it is 0.0625". The back pressure is proportional to the inverse 4th power of the diameter, so the back pressure for the newer wells will be at least 256 times higher than for the older wells for tubes of the same length.

To eliminate the problem of the back pressure an auxiliary pump is used to fill a Tedlar bag with sample gas. The PAR sample is taken from the Tedlar bag, at ambient pressure, so there is no back pressure whatever. The hold time for the Tedlar bags is 8 hours, due to the permeability of the Tedlar for different chemicals of interest. The bags should not be reused. If reused certain constituents tend to be concentrated by adsorption onto the walls of the bag.⁷ The data for all wells beginning in the first quarter of 1995 were taken using the Tedlar bag technique.

In one test long runs of plastic tubing connected the instrument to the well. In ground water sampling the materials used must be chosen not to influence the test.⁸ Similarly in pore-gas sampling. On tubing runs of up to 50 ft effects as large as 30% were noticed. That is when Tygon ® tubing was used as much as 30% of the TCA was absorbed in the tubing. There was no detectable effect when either pure teflon or teflon lined tygon was used.

Plumbing leaks can be a constant source of consternation. If any of the plumbing leaks, diluting the sample, errors result. The actual volume drawn into the sorption sample for the TDGCMS is measured directly by the mass flow integrating meter. The sample provided to the PAR is drawn into a Tedlar bag so it is important that there be no leaks in the plumbing that leads to the bag thereby diluting the sample. If the sampling manifold has a small leak its effect is magnified if a large pressure difference must be applied to withdraw a sample from the well, as is the case, for example, on the new SEAMIST equipped wells. Leak rates lower than 2.5 Torr per minute (leak rate measured from a base pressure of 250 Torr) are maintained on the sampling plumbing. It is not easy to do much better than this with plastic tubing and many joints and connections.

DESCRIPTION OF THE FIELD UNIT

Both the PAR and TDGCMS sampling unit can be mounted in the back of a pickup for ease of sampling. The truck can be driven to the wellhead and the various ports connected sequentially to the manifold. Power for the PAR is provided by a 12v dc to 120v ac inverter run from the truck battery. The vacuum pump is a Gasprobenheimer GS 212 sampling unit which has its own flowmeter and volume measuring gauge. It is made by Desaga, a German company. The TDGCMS sampling unit runs directly from the truck's 12v battery.

So far the equipment has been operated in a temperature range from -10 degrees to 140 degrees Fahrenheit. At the low end the o-rings get brittle and seals fail. Just before sampling the o-rings can be warmed in the hand to improve the seal. The liquid crystal display for the flowmeter on the TDGCMS sampling unit fails at both the low and high end of the temperature range. The pump in the PAR begins to have difficulty operating below about 40 degrees F. The PAR has operated at 140 degrees F with no complaints. The TDGCMS unit is not water resistant.

CONCLUSION

In conclusion we hope the lessons learned will spare someone else from making the same discoveries we made and it will speed them to accurate analyses. Concentration measurements of volatile organics are enhanced by using both TDGCMS and PAR. While the TDGCMS is sensitive to 50 analytes, the PAR is best when looking for no more than 5. The PAR technique offers an advantage in the field because results are known immediately. TDGCMS analysis takes a minimum of 6 weeks.

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