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RAPID SURFACE SAMPLING AND ARCHIVAL RECORD SYSTEM (RSSAR)

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ABSTRACT

The objective of this work is to develop a surface sampling device that will enable quick characterization of concrete and steel surfaces. A bulk sampling oven is also being developed which will enable characterization of loose bulk debris that is sized to 1 cm^3. The sampling device consists of a sampling head (steel or concrete), a quick look detector, and an archiving system (sorbent tube). The sampling head thermally desorbs semi-volatile contaminants, such as polychlorinated biphenyls, oils, and other organics, from concrete and steel surfaces. The volatilized materials are passed through a quick-look detector and an indication of the presence or absence of contamination is given. The sensitivity of the quick-look detector can be attenuated for various levels of contaminant sensitivity. Volatilized materials are trapped in a tube filled with an appropriate solid phase adsorbent. The tubes are housed in a magazine which also archives information about the sampling conditions such as air flow rates, sampling temperatures. A more detailed and automated analysis of the tubes can be done at a later date by transferring the magazine to a thermal desorption instrument.

The concrete sampling head is fitted with a tungsten-halogen projection lamp that is rated for 1000 Watts of power. The concrete sampling head has been tested on concrete spiked with model contaminants. In laboratory experiments the concrete sampling head extracted model contaminants by heating the top 4 mm of the surface to 250 °C within a sampling period of 100-200 seconds. Flow rates were 60-100 ml/min.

The steel sampling head has been tested in the laboratory on different types of steel (rusty, carbon, stainless) and has extracted model contaminants from the surface of the metal within a period of 30 seconds.

The bulk sampling oven has efficiently (>70%) volatilized model contaminants that were placed into the oven tray. The oven was operated at 250°C. This temperature was sufficient to volatilize and transfer model contaminants from the oven compartment to a solid phase adsorbent.

A mathematical model of heat and mass transport in concrete has been developed and applied to the process of rapid thermal desorption of contaminants from concrete. It has been shown that the presence of moisture plays a significant role in the efficiency of contaminant removal. A maximum rate of contaminant removal occurs when the moisture content is about 100 kg m-3. Significant pore pressures resulting from steam generation and gas expansion are predicted.

The bulk sampling oven and the concrete and steel sampling heads will be useful during decontamination and decommissioning operations. The sampling system will provide real-time data so that the lag time between sampling and analysis will be reduced from weeks to real-time. Other benefits from this system include reduction of workers exposure to solvents, minimal waste generation and reduced dollars spent on the analysis of clean samples.

INTRODUCTION

The purpose of this effort is to develop a rapid surface contamination measurement system that will provide a “quick-look” indication of contaminated areas, an archival record, and an automated analysis of that record. By providing rapid analyses and a large number of accurate measurements of surface and subsurface contamination, the cost of remediation of large industrial sites will be dramatically lowered by reducing both the characterization time and the material fraction that must be remediated.

The Department of Energy (DOE) sites contain very large areas contaminated with radionuclides and semivolatile organic compounds as the result of decades of nuclear weapon and fuel production activities. Concrete, transite, and metal surfaces have been exposed to these contaminants. Unknown but substantial portions of these surfaces have been contaminated to various depths. Because contamination concentrations can vary widely over adjacent exposed surfaces, these surfaces must be sampled at closely spaced intervals to provide accurate identification of contaminants. Consequently, a huge number of surface regions must be characterized, particularly because remediated areas must be sampled more than once for identification and verification.

Current surface characterization procedures are difficult, expensive, and slow. They require an unacceptably long time to perform and consume a large share, often around 30%, of remediation/disposition resources. Accordingly, they will not meet the challenge of providing low-cost, rapid, quantitative and certifiable surface characterization on the scale required by the DOE as part of its decontamination and decommissioning activities.

"Concrete," bulk, and "steel" sampler heads are being developed to handle the most frequent sampling requirements. A concrete surface sampler, which has been developed and demonstrated, can be used to determine contamination levels at surfaces and down to a few millimeters below the surface for porous, low thermal-conductivity materials, providing information also targeted by the standard wipe test. A bulk sampler head has been developed and demonstrated that can be used to measure contaminants in asbestos, paint scrapings, particulate waste, and samples from drilling as well as calibration standards. To determine subsurface contamination, samples from drilling would be placed in the bulk sampler head connected to the RSSAR system for "quick look" and archival analyses. A steel sampler head has been designed for the markedly different sampling conditions provided by nonporous surfaces with high-thermal conductivity.

The purposes of the "quick-look" module are to provide a real-time guide of sampling strategy, a real-time practical indication of system performance, a personnel safety indicator, a redundant indicator channel, and a method to reduce the fraction of samples that are subjected to more time-consuming detailed analysis. The viability of "quick-look" has been demonstrated using both a photoionization detector and ultraviolet absorption.

The archival multisample trapping module traps contaminants and stores them for detailed analysis. This stored record, organized in a cassette format (as shown in Figure 1), is associated with corresponding sample information, to facilitate record-keeping, to minimize handling and training requirements, to reduce errors caused by operator fatigue in the highly repetitive sample acquisition and analysis tasks, and to expedite automated readout. A single sample trapping module was tested initially and the results were used in the design and fabrication of an archival multisample trapping module. The archival multisample trapping module allows trapping of up to 50 separate samples and transfer to a modified thermal desorption autosampler for subsequent analyses.

The thermal desorption autosampler accepts the organized record format and provides an automated interface to alternative readout instruments such as gas chromatography/mass spectrometry, tandem mass spectrometry, gas chromatography with electron capture detector, or a fast optical readout such as a photo-ionization detector. By manipulating sample and substrate size, quantities of PCBs of interest to the DOE (10 μg on 100 cm^2 surface) should easily be detectable with little additional optimization of techniques that have been developed.

The overall RSSAR System is modular and will use accurate sample acquisition, handling, and analysis techniques. The availability of an archival record that allows detailed analysis (and an occasional backup check on the quick-look detector) will expedite material disposition planning and regulatory approval. Consequently, the RSSAR System should provide a cost-effective approach for the measurement of semivolatile contamination required for large industrial site remediation.

RESULTS

Concrete Sampling

A prototype concrete sampling head was developed based on results from field testing of initial concepts and Monte Carlo simulations of illumination patterns. The concrete sampling head uses a one thousand watt tungsten halogen lamp as the heat source located near the top of a smooth reflective hemispheric housing to provide more efficient coupling and minimize hot spots on the surface. A diffuser plate is located just below the lamp with a protective window at the bottom. Vapors are collected through eight slots in the lower chassis which are connected to a recessed channel in the heating block. Figure 2 shows a cross-sectional view of the concrete sampling head.

Results from thermal testing of the modified concrete sampler using an imaging radiometer are shown in Figure 3. Uniform temperatures were achieved at over 60 % of the heated surface with another 15 to 20 % of the area at temperatures close to the uniform area.

Tests were conducted on prepared concrete specimens previously spiked with known concentrations of anthracene, 2,4,5- trichlorobiphenyl, and phenyldodecane as surrogates for polyaromatic hydrocarbons, polychlorinated biphenyls, and oil, respectively. Results which are shown in Figure 4 indicate that thermal sampling is able to correlate well with bulk contamination levels. The essential elements of the RSSAR process including the semiquantitative performance of a quick-look detector, trapping of desorbed contaminants, efficient transfer to a gas chromatography column, and close quantitative correlation between concentration determinations and original bulk contaminant loadings gave positive results in these experiments.

Thermal Modeling

A mathematical model of heat and mass transport in concrete has been applied to the process of rapid thermal desorption of contaminants from concrete. It has been shown that the presence of moisture plays a significant role in the efficiency of contaminant removal. The simulated water contents ranged from 0 to 1000 kilograms per cubic meter, and the permeabilities extended from 10^{-17} to 10^{-15} m^2. The model indicates that the removal of PCBs is fairly insensitive to moisture content as long as the moisture content is between 50 and about 400 kilograms per cubic meter as shown in Figure 5. At lower moisture contents, the reduced amount of steam available for stripping the PCB vapors out of the concrete decreases the removal rate. Maximum contaminant removal occurs when the moisture content is about 100 kg per cubic meter. At higher moisture contents, the increased latent heat requirements reduce the heating rate and hence the PCB removal rate.

The model also indicates that highly permeable concrete is expected to have higher PCB removal rates, with other conditions being the same as shown in Figure 6. In a 30 second simulation, concrete with an intrinsic permeability of 10^{-15} m^2 had twice the removal of PCBs than concrete with 10^{-17} m^2 permeability. While the relation between removal rate and permeability is much weaker than linear, the fact that the local permeabilities within a real concrete specimen can vary by several orders of magnitude make this effect significant. Extension of these results to heterogeneous concrete would suggest PCBs would be removed preferentially from regions containing microcracks rather than uncracked regions.

Bulk Sampling Head

A bulk sampling head was developed for analysis of drill cuttings, pulverized concrete, soil, and particulate waste. The sampler was made from a solid aluminum block heated with a 700 watt calrod heater. The sampler was connected to the quick-look module through insulated tubing and swagelock fittings. The bulk sampling head was used extensively for testing of commercial sorbents for their ability to trap the target contaminants. Five different adsorbents, Carbotrap 370, Tenax GR, Carbopack B, Carbopack C, and XAD-2, were evaluated for their efficiency to trap the model contaminants anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane both in the presence and absence of water. Carbotrap 370® was found to have the best performance with recoveries ranging from 77.8% to 100%. The results from thermal recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane with the screened adsorbents are reported in Table 1.

Steel Sampling Head

The metal sampler head has undergone initial testing with an arc lamp. Total lamp power output and output through the delivery line were measured at various lamp inputs. Results to date are shown in Table 2. These powers were measured with a high power calibrated thermopile detector, which responds essentially uniformly to UV, visible and infrared wavelengths.

Coupling efficiencies into the delivery system are lower than expected. Actions to increase coupling efficiency from the present 20% level to near 50% are underway.

A thin (1.2 mm thick) rusty carbon steel sample with a tack welded thermocouple on the back end was illuminated with the steel sampler at room temperature and lamp power set at 600 watts. The approximate surface temp of the sample reached 205 °C in 30 seconds following the time dependence shown in Table 3. Thinner metal samples heat up more quickly while thicker specimens take longer to reach proper sampling temperatures.

The steel sampling head has been tested in the laboratory on different types of steel (rusty, carbon, stainless). A test solution was prepared so that the concentrations of model contaminants-anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane- was approximately 1.0 µg/µl. Various amounts of this solution- 15, 20 or 25 µl- was spiked onto stainless steel, rusty steel and carbon steel test coupons. Recovery of the test compounds from 4-mil-thick carbon steel was shown to occur within 30 seconds with radiant heating of the steel surface. The data for the recovery of anthracene, 2,4,5-trichlorobiphenyl, and phenyldodecane from carbon steel is shown in Table 4. For 4-mil thick carbon steel sampled using radiant heat for 2 seconds, recoveries of model contaminants ranged from 71% to 93% with an average of 82%. Optimum recoveries from 4-mil-thick stainless steel required a 3 second sampling with radiant heat and yielded recoveries ranging from 60% to 100% with an average of 81%. Rusted steel was more difficult to sample but generally yielded recoveries ranging from 50% to 100%.

Multisample Trapping Module and Thermal Desorption Unit

A fully automated, modular, and versatile concept has been developed for the Multisample Trapping Module (MSTM) portion of the RSSAR system. The concept will allow for RSSAR operations to be conducted with minimal operator input and virtually no operator handling of individual samples. Sorbent tubes will be housed in a transportable magazine that will interface to both the RSSAR system and the Thermal Desorption unit (TDU) system. Samples will be protected prior to, and subsequent to, sampling to minimize contamination and cross-contamination potential. During sampling, sensors will monitor all relevant parameters to ensure reliable, accurate samples. Data generated from sensors during sampling and RSSAR quick-look detector results will be stored in nonvolatile electronic memory resident in the sorbent tube magazine. The data will then be available to the TDU and analytical instruments to facilitate timely and accurate analysis. Interface to the Perkin-Elmer TDU requires a sample transfer device that resides on top of the ATD-400. The RSSAR system will have the capability to perform both quick-look detection and sorbent tube sampling at each location. However, a sorbent tube sample is not required for each location. Sufficient memory exists in the magazine to store data for all 50 archived sorbent tube samples plus 500 quick-look sampling points.

CONCLUSIONS

Concrete, steel, and bulk sampler heads for characterization of contaminants on metal, steel and loose bulk debris have been designed, built, and thermally tested. An archival multisample trapping module was designed, built, and tested. Testing of the components was conducted on concrete and on three different types of steel- stainless, carbon, and rusty steel. Results from testing of the RSSAR system indicate that the basic concept of using thermal desorption for sampling of various semivolatile organic contaminants from building surfaces and materials is viable. Sampling of model contaminants representing polychlorinated biphenyls, oils, and polyaromatic hydrocarbons resulted in sufficient recoveries of contaminants to assess building contamination levels in a much more representative manner than current technology wipe samples.

ACKNOWLEDGMENTS

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CONTRACT INFORMATION

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Table 1. Percent Recovered by Thermal Desorption[1]

Sorbent	Load (ug)	Anthracene	2,4,5- TCB	Phenyldodecane
Carbotrap 370	10	77.8	86.1	78.7
Carbotrap 370	20	81.3	83.6	79.5
Carbotrap 370[2]	40	85.0	82.4	80.7
Carbotrap 370[2]	20	87.2	87.4	84.4
Carbotrap 370[2]	20	101	100	96.2
Tenax GR	10	79.2	80.1	81.3
Tenax GR	20	106.4	93.1	78.6
Tenax GR	40	55.8	70.8	65,3
Carbopack B	10	85.4	98	85.7
Carbopack B	20	91.7	91.6	81.9
Carbopack B	40	53.1	55.6	47
Carbopack C	10	47.8	81.8	51.9
Carbopack C	20	57.4	86.2	68.2
Carbopack C	40	10.3	85.9	11
XAD-2	10	1.5	0	0
XAD-2	20	89.6	88.9	85.8
XAD-2	40	51.4	50	50.7

[1] Average of two trials
[2] Numbers obtained from one run

Table 2. Steel Sampling Head Power Delivery

Lamp Power Setttting	Power Into Delivery System	Delivery System Output
400 W	120W	26W
600W	205W	42.5W
800W	295W	59W

Table 3. Steel Sampling Head Sample Temperature with Time

Time (sec)	Temperature (°C)
0	21.7
5	80.5
15	143.2
30	204.8
45	243.9
60	287.2

Table 4. Recovery of anthracene, 2,4,5-trichlorbiphenyl, and phenyldodecane from a 4-mil thick carbon steel thermally desorbed by the steel sampling head (2 sec irradiation)

Carbon steel test volume	Model compounds	Theoretical recovery (µg)	Measured recovery (µg)	Percent recovered
15 µl test solution	anthracene	16.5	13	79
	2,4,5-TCB	15	13.9	93
	phenyldodecane	21	18.2	87
15 µl test solution	anthracene	16.5	15.3	93
	2,4,5-TCB	15	13	87
	phenyldodecane	21	17.4	83
20 µl test solution	anthracene	22	17.6	80
	2,4,5-TCB	20	17.9	90
	phenyldodecane	28	23.5	84
20 µl test solution	anthracene	22	16.3	74
	2,4,5-TCB	20	16.4	82
	phenyldodecane	28	20.6	74
25 µl test solution	anthracene	27.5	19.4	71
	2,4,5-TCB	25	20.6	82
	phenyldodecane	35	26.9	77
25 µl test solution	anthracene	27.5	24.0	87
	2,4,5-TCB	25	20	80
	phenyldodecane	35	27	77
blank	anthracene	0	0	0
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0
blank	anthracene	0	1.4	-
	2,4,5-TCB	0	0	0
	phenyldodecane	0	0	0

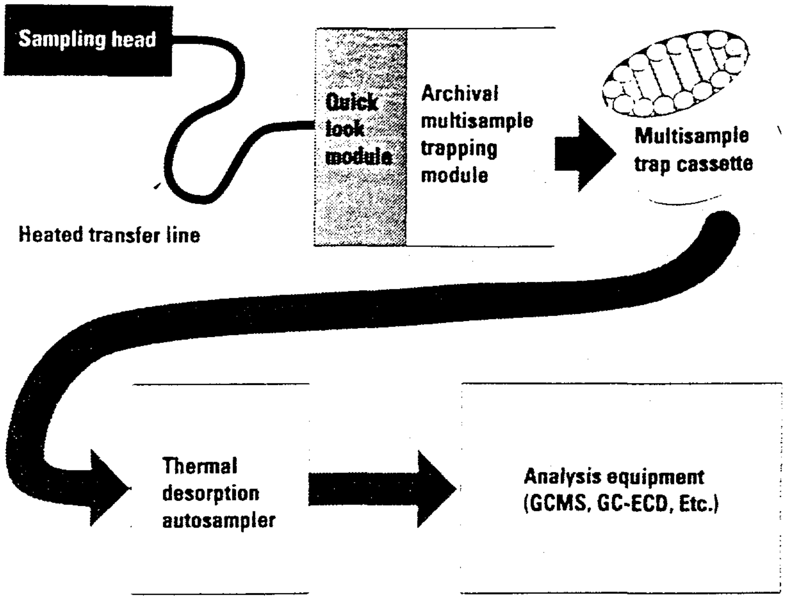

Figure1. Configuration of the RSSAR System. The system includes sampler heads, a "quick-look" detector, an archival record, and an automated interface to couple this record into various types of analysis equipment.

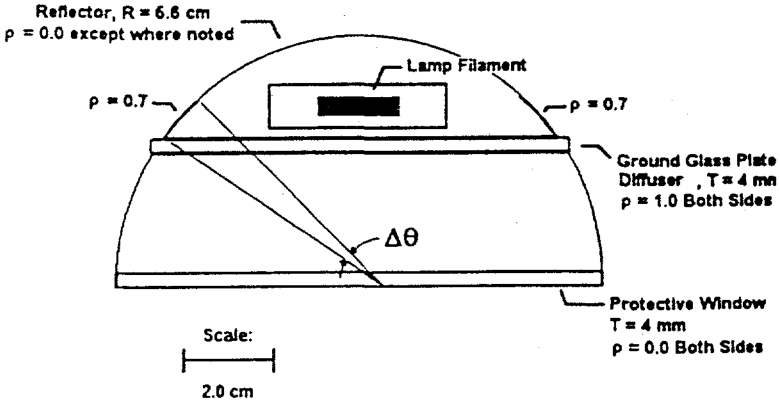

Figure 2. Concrete sampling head cross section.

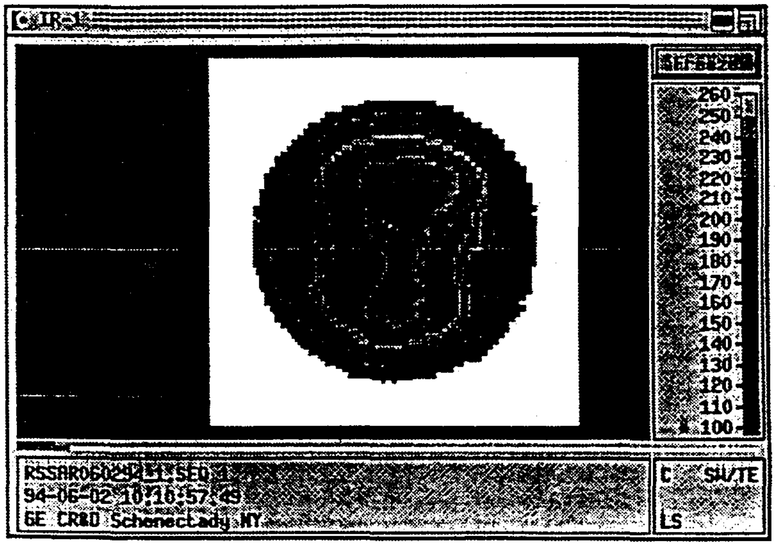

Figure 3. Concrete sampling head temperature distribution. The peak temperature shown in the two small regions of the upper central lobe is between 230 and 240 °C.

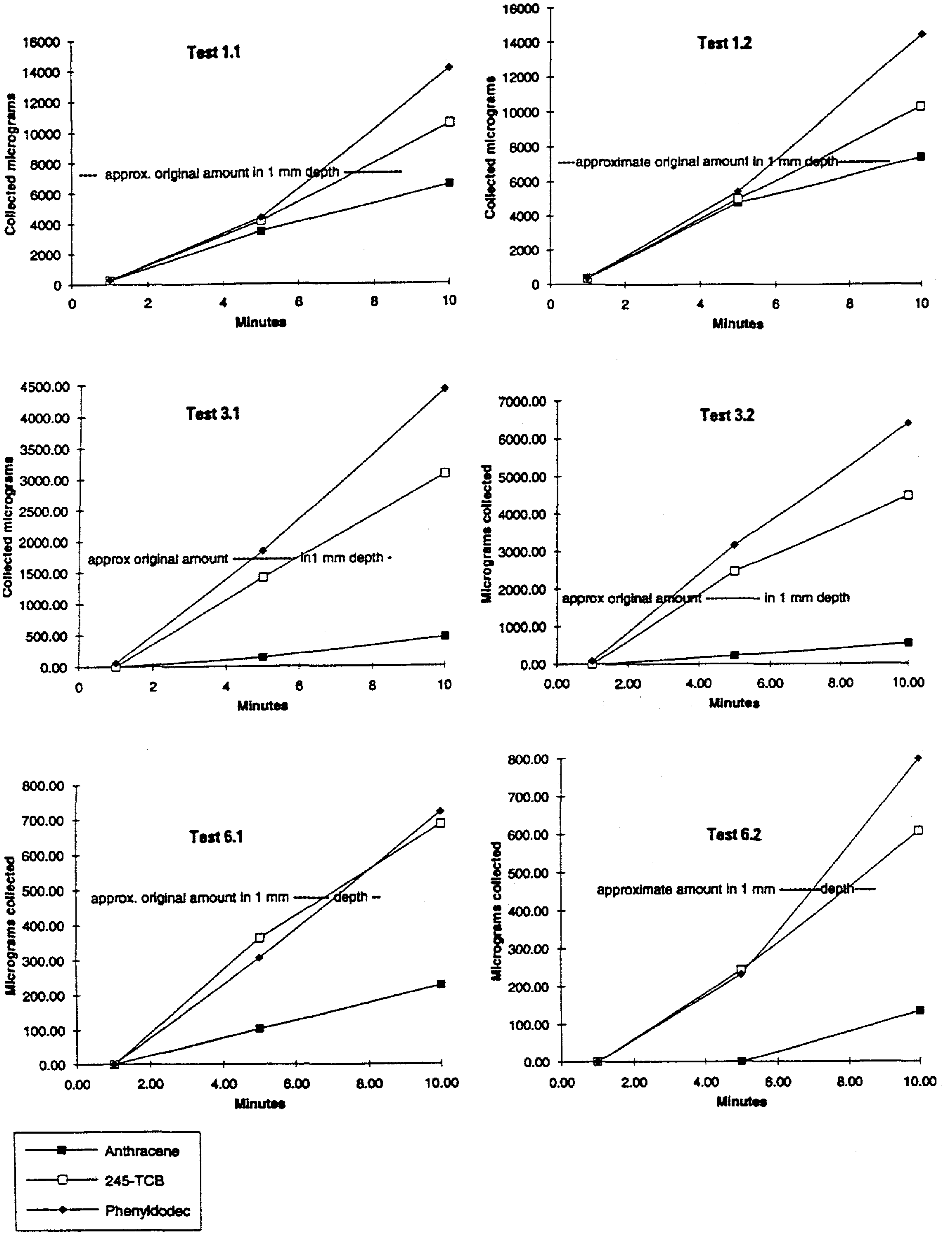

Figure 4. Total contaminant extraction amounts vs. time determined from GC analysis of solvent traps.

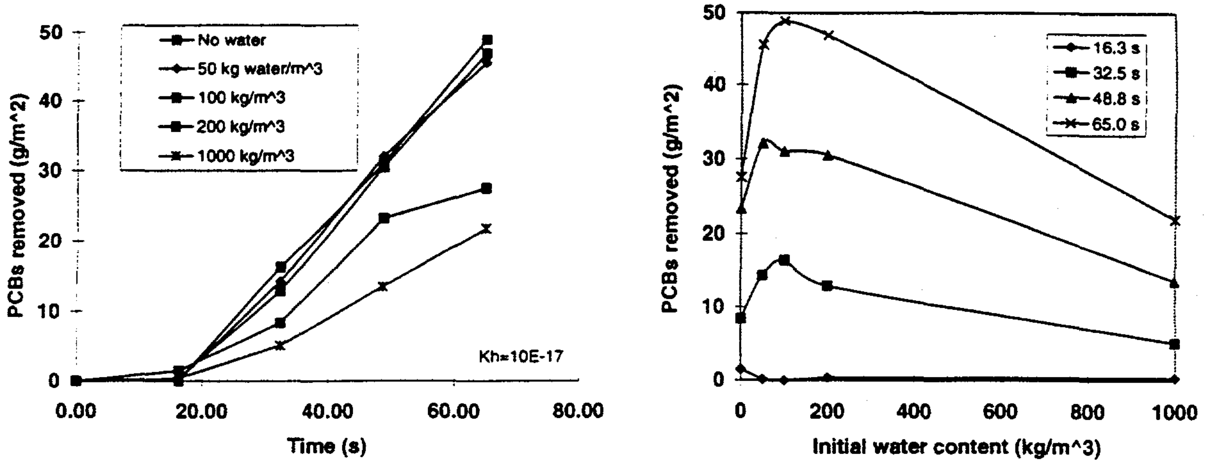

Figure 5. Thermal modeling of effect of moisture content on PCB removal.

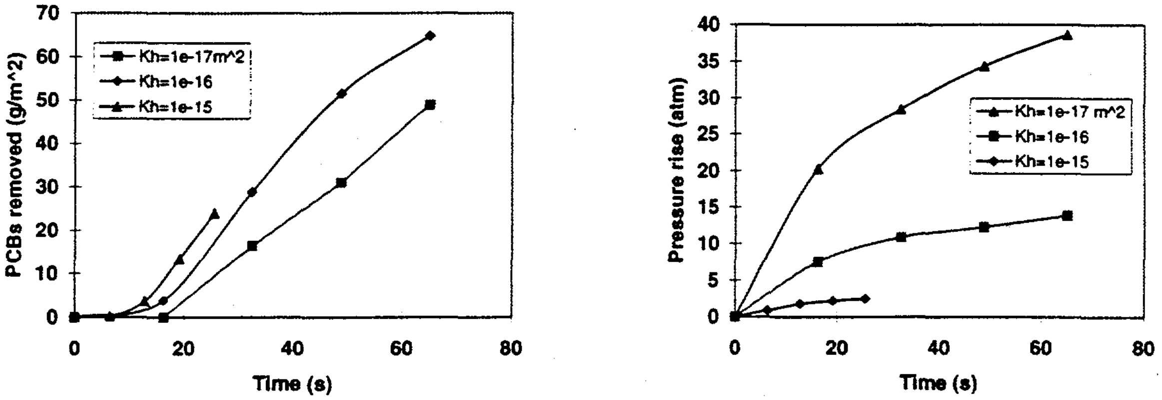

Figure 6. Effect of permeability on PCB removal.