Thermal Desorption Gas Chromatography-Mass Spectrometry Field Methods for the Detection of Organic Compounds

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INTRODUCTION

The overwhelming amount of information required to characterize purported hazardous waste sites, *as well as* to support Superfund site cleanup and closure activities, have catalyzed the development of field instrumentation capable of providing site managers with immediate access to chemical and physical data. The demand for field "practical" methods and instrumentation has been recognized by the U.S. Environmental Protection Agency (1, 2).

Faster data turnaround times and ease of operation have been the primary motivation for selecting *field* gas chromatographic (GC) methods of analysis. Despite recent advancements in field GC instrumentation, typical applications focus on the detection of EPA listed volatile organic compounds (VOCs) in water, air, or soil gas. The primary limitation of commonly employed field GC's is the non-definitive signal response of the detectors (including photoionization, flame ionization, thermal conductivity, and electron capture) which are incapable of providing unambiguous identification of the wide variety of organic compounds that may be present in a highly contaminated sample. Generally, ten to twenty percent of the samples analyzed on-site are "split" for confirmation by GC with mass spectrometric (MS) detection. Since most commercially available mass spectrometers have traditionally been housed and operated in a clean air, temperature controlled room and the notion that economies of scale require highly trained MS operators to be based in multi-MS laboratories, misapprehensions have arisen as to whether MS's can be operated successfully (and profitably) in the field.

The limited availability of field GC-MS's is not a function of MS operating requirements, but more, the perception that significant sample cleanup and QA/QC procedures will be required to obtain useful data as well as the apparent reluctance of instrument manufacturers to enter the field marketplace. Until recently, these misconceptions have perpetuated the myth that GC-MS's belong solely in the laboratory.

Over the last several years, we have discussed field GC-MS applications utilizing Bruker Instruments' mobile mass spectrometer (2-6). The MS, initially designed for NATO as a chemical warfare detector, was manufactured from the outset as a field instrument. In our studies, the MS was transported from site-to-site in a mid-sized truck and was battery operated for ~ 8 to 10-hr at ambient conditions. For example, samples have been analyzed with outdoor conditions, where; temperatures have been between 10 °F and 90 °F, rain, snow, and high humidity. Gas cylinders were not necessary for GC operation since charcoal filtered ambient air served as the carrier gas.

Simple field methods have been developed based on analyte introduction by thermal desorption (TD) followed by *fast* GC separation and MS detection. Screening level and more quantitative TDGC-MS methods have been submitted to EPA's EMSL-Las Vegas for VOCs in water, soil/sediment, soil gas, air *and* polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in soil/sediment for inclusion into the compendium of field methods that will be published by EPA's Analytical Operations Branch. The methods include a menu of QA/QC procedures whose implementation depends upon a given study's objectives. The goal is to provide a practical GC-MS tool that can deliver the quality of data required for the study with minimal sample cleanup. Presented in this paper are typical examples of data quality *and* a comparison of field and laboratory results one can expect from both the screening and more quantitative field TDGC-MS methods for PCBs, PAHs, and pesticides.

EXPERIMENTAL SECTION

A mobile mass spectrometer (Bruker Instruments, Billerica, MA) was used in these studies. The TDGC-MS was powered by battery or electrical supply from the site. The MS was transported to Superfund sites in Westborough (Hocomonco Pond; PAHs) and

North Dartmouth, MA (Resolve; PCBs) in a Chevrolet Blazer. In addition to the instrument's internal data collection and monitoring system, the MS was equipped with an external data system and thermal desorption sampling probe. Sample introduction was made by thermally desorbing (TD) the analyte directly from soil/sediment *or* from an organic extract through the TD sampling probe's (SP) short 3.5 m fused silica capillary column. For direct TD soil/sediment experiments, 0.5 g of soil was placed on an aluminum foil covered petri dish. An internal standard was injected into the soil before the measurement was made. In contrast, the more quantitative measurements required several additional steps: 1) 0.5 g of soil was weighed and extracted with 2 ml of solvent; 2) prior to extraction, a known quantity of surrogate (or target) compound(s) was added to the soil (or field blank) to determine extraction efficiencies (note: this step was required since a single 2 ml extraction yielded analyte recoveries of less than 100%; 3) co-inject known aliquots of extract and internal standard onto aluminum foil covered petri dish; 4) thermally desorb analyte. Shown below are the TDGC-MS operating *and* PCB, PAH, and pesticide experimental conditions:

Operating Conditions

Mass Spectrometer	Bruker Instruments (Billerica, MA)
electron energy	70 volts (nominal)
mass range	45 to 400 amu
scan time	2 sec
MS tune	autocalibrate ($H_2O_{(g)}$; FC-77); 18, 69, 119, 169, 331 amu
mass resolution	set to unity; ca. 10% valley definition
ion detection	17 stage Cu-Be dynode electron multiplier with self-scaling integration amplifier (10^8 linearity)
Sampling Probe Head	260 °C
GC Column	DB5 (J & W Scientific, Folsom, CA)
dimensions	3.5m x 0.32mm i.d.; 0.25μ film thickness
carrier gas	ambient air purified through carbon filters
flow rate	3 to 4 ml/min

	PCBs	PAHs	Pesticides
initial temp	140°C, 30 sec	70°C, 40 sec	120 °C
temp prog	120°C/min	35°C/min	17°C/min
final temp	200°C, 90 sec	233°C, 80 sec	233°C
Internal Standards	d_{10}-pyrene	d_8-naphthalene or d_{10}-pyrene	d_{10}-phenanthrene
solvent extraction	C_6H_{14}	CH_2Cl_2	C_6H_{14}

Data were acquired by using the internal monitor's selected ion monitoring program. The data system reported the total ion current as a logarithmic value. The antilog value is used in conjunction with MS response factors and analyte recoveries to calculate concentrations in the sample. Standards were purchased commercially from the following companies: PCBs (Ultra Scientific, Hope, RI); PAHs (Supelco, Inc., Bellefonte, PA); Pesticides (Chem Service, West Chester, PA); internal standards (Cambridge Isotope Laboratories, Woburn, MA). All standards and soil recovery experiments were prepared with high purity solvents (> 96 %) as received.

RESULTS and DISCUSSION

The objective of this study was to develop *fast* TDGC-MS methods (< 20 min/sample including sample cleanup). Two methods were developed. Analyte introduction for quantitative measurements were made by co-injecting organic extracts (or standard solutions) of PCBs, PAHs, or pesticides and internal standard(s) onto an aluminum covered petri dish followed by TDGC-MS and for screening measurements by direct thermal desorption from soil/sediment.

The surface monitor program mode was employed in this study. Target compounds (maximum number twelve) were detected by selected ion monitoring (SIM) MS. The (logarithm) ion current was recorded and displayed visually on the system's monitor. Found in Figure 1 are typical PCB and pesticide outputs. Three fragment ions representative of each compound(s) and an impossible ion (see below for rationale) were selected for detection. For example, in cell A the target ions and their relative intensities for the three monochlorinated PCBs were 188 (100%), 190 (33.5%), 152 (31.1%), and 189 (0%). Similarly, cells B-H in Figure 1a illustrate the SIM four ion current responses for chlorination levels 2 - 8, respectively; cell I, d_{10}-pyrene (internal standard); cells J - K, PAH surrogates; and cell L, hydrocarbon signals indicative of matrix complexity. Detection was made, and printed on screen, when the signals from the four ions relative to each other agreed to within preset criteria over a predetermined retention time window. In this mode, SIM response may be considered analogous to selective GC detection. Note above, that the last fragment ion for the monochlorinated PCBs had a relative intensity of 0%. Inclusion of an impossible ion served to provide selective detection. For example, an increase in fragment 1 ion current relative to fragments 2-4 within the target compound's retention window precluded compound identification. Thus, the mathematical algorithm assisted in screening out interferants present in the sample.

The *fast* GC linear temperature programs and MS detection provided sufficient separation to identify compound(s) as shown in Table 1. Figure 2 is a typical instrument print out for the amount (4-ion total current count, in log values, left vertical axis) vs. time response curves (horizontal axis) for four of the chlorinated pesticides shown in Figure 1b. In addition to the compound and amount detected, other information visible on the display included "real-time" monitoring of: logarithm of ion current, left vertical axis; MS vacuum pressure, right vertical axis; and column temperature, above right vertical axis.

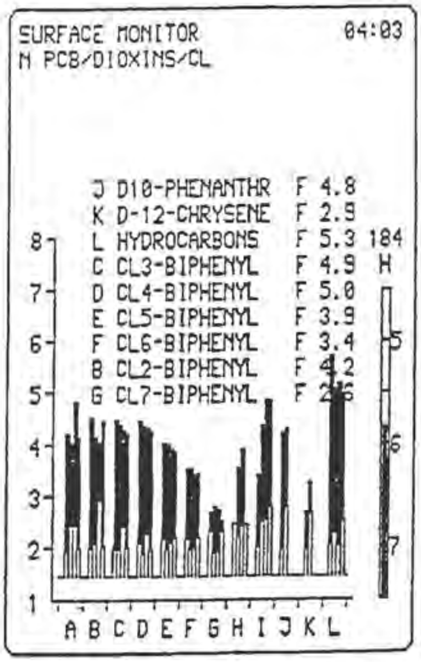

Figure 1a

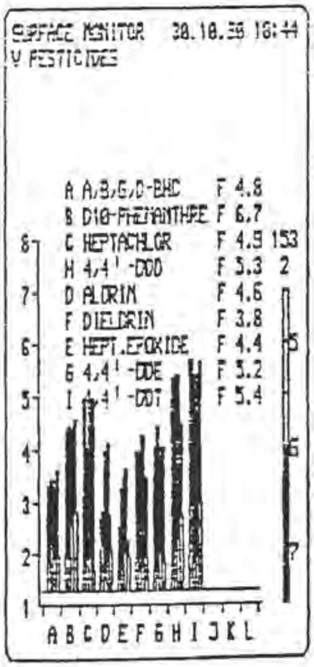

Figure 1b

Figure 1. Typical Field TDGC-MS SIM response of a standard solution containing PCBs (1a) *and* chlorinated pesticides (1b).

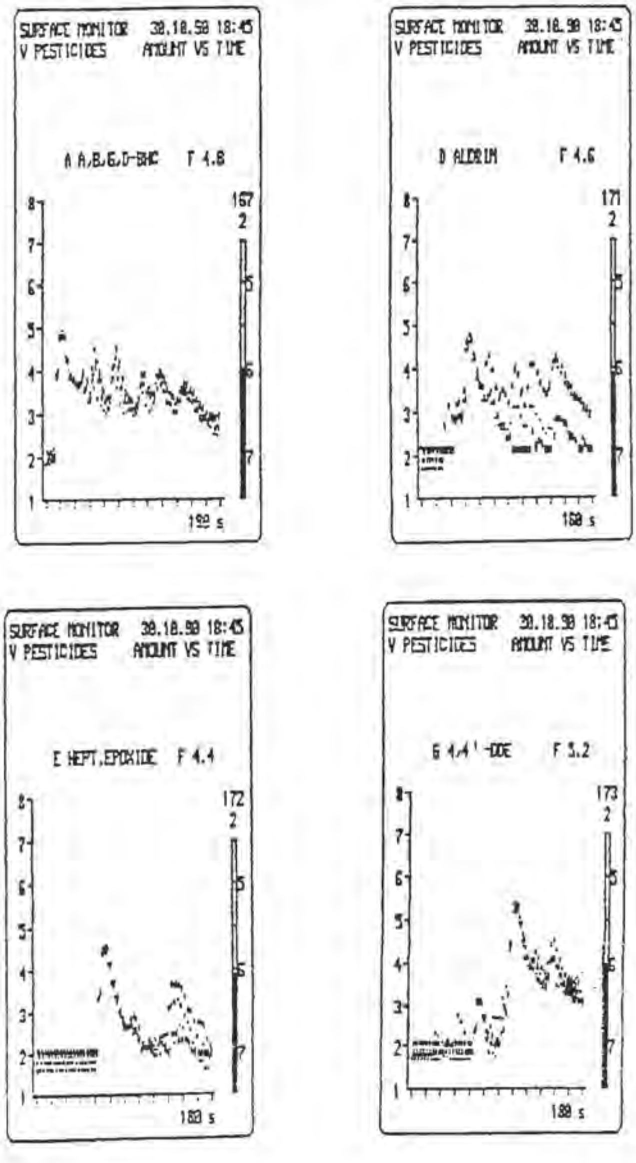

Figure 2. Amount versus time curve for several chlorinated pesticides shown in Figure 1.

TDGC-MS experiments were performed between the concentration range of 40 and 4000 ng/compound. Repetitive measurements at each concentration yielded differences in the log value of ± 0.1, producing ion current differences of less than 30%. Table 1 lists typical response factors (RF) and percent relative standard deviations (%RSD) calculated for PCBs, PAHs, and pesticides thermally desorbed from an organic extract. Plots of signal versus concentration were linear (r= 0.999) with the %RSD for the average RF less than 30%, meeting initial and continuing calibration criteria in the Contract Laboratory Program. Table 2 lists representative RF and RSDs for PCBs and PAHs thermally desorbed directly from soil. Despite somewhat larger percent RSDs for some PAHs, measurement precision at this level will only be critical at site cleanup "action" levels. It should be pointed out that thermal desorption extraction efficiencies differ greatly for some PAHs (see Table 3 for minimum detectable quantity. Note: RF in Table 2 calculated over linear range as shown in Table 3). Minimum detection levels for most compounds were ~ 1 ppm for soil/solvent extraction and slightly higher for direct soil thermal desorption. Because TDGC-MS experiments can be performed in 5 to 20 min depending on the method employed (with known data quality), many more analyses can be performed than currently practiced for site characterization, stockpiling, and worker/community protection activities. The frequency for performing continuing calibration checks may be determined (on-site) by following surrogate compound RF values (see below).

Research has shown that compound recoveries vary with soil-type. For example, PCB/hexane (0.5 g/2 ml hexane, 2 min) extraction recoveries were 69 ± 5% for 50 ppm backyard (organic) soil, 80 ± 2 %, for 25 ppm sandy material from the Resolve Superfund site in North Dartmouth, MA, and 73 ± 5 % for an ERA, 35 ppm, soil. Therefore, appropriate surrogate compound(s) and/or target standards must be added to samples as the soil-type varies. Such experiments can be used to determine instrument performance as well.

Tables 4 - 7 illustrate typical examples of data quality one can expect from the field TDGC-MS methods. Split samples were collected by EPA's Region 1 oversight contractor *and* analyzed in the field (Tufts) and lab (Lockheed ESC, Las Vegas, NV). Table 4 compares field and lab GC-MS measurements for total PCB present in several samples obtained from the Resolve site while Table 5 delineates chlorination level comparisons for two of the samples. The field and lab results are in excellent agreement.

Shown in Tables 6 and 7 are field and lab comparisons for four PAH samples from the Hocomonco Pond (Creosote contaminated Superfund) site. Note that the samples in Table 6 and the sample labeled HP-SB5 in Table 7 were performed by SIM using the system's internal monitor as described above. In contrast, the sample labeled pond (Table 7) was analyzed by total ion current, selected ion monitoring extraction. The advantage of this detection method was that full mass spectral fragmentation data and compound library matching was applied. On the other hand, the disadvantage was that ion current from matrix components may add to the SIM signal resulting in higher concentrations than what might actually be present. This, however, is no different than what can occur using traditional CLP, MS methods. Field and lab comparisons for PAH samples also appear to be in good agreement.

Additional data will be presented describing further application of the field TDGC-MS methods. Illustrations will be given documenting cost effectiveness. Results will show that GC-MSs can be operated in the field, provide rapid access of data, and allow project managers to make decisions on-site.

ACKNOWLEDGEMENTS

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Table 1. Thermal Desorption Field GC-MS Response Factors and Percent Relative Standard Deviations - from Extract (Quantitative Method)

Polychlorinated Biphenyls

Chlorination Level	Ave RF(n=5)	% RSD
Cl-1	0.47	20
Cl-2	0.26	17
Cl-3	0.27	17
Cl-4	0.16	15
Cl-5	0.15	12
Cl-6	0.10	15
Cl-7	0.06	17
Cl-8	0.03	10

Polycyclic Aromatic Hydrocarbons

naphthalene	1.37	12.3
acenaphthylene	8.63	12.3
acenaphthene	0.82	24.8
fluorene	0.58	12.3
phenanthrene/anthracene	4.59	12.3
fluoranthene/pyrene	9.52	9.5
chrysene/benz(a)anthracene	0.90	13.3

Chlorinated Pesticides

BHCs	0.10	9.6
Heptachlor	0.02	23.5
Aldrin	0.07	16.3
Heptachlorepoxide	0.03	10.9
Dieldrin	0.02	25.4
4,4'-DDE	0.32	16.3
4,4'-DDD	0.16	18.6
4,4'-DDT	0.12	19.7

Table 2. Thermal Desorption Field GC-MS Response Factors and Percent Relative Standard Deviations - Direct from Soil

Polychlorinated Biphenyls

Chlorination Level	Ave RF(n=5)	% RSD
Cl-1	13.44	19
Cl-2	3.75	25
Cl-3	3.91	23
Cl-4	2.55	16
Cl-5	2.02	16
Cl-6	1.61	16
Cl-7	1.04	23
Cl-8	0.36	19

Polycyclic Aromatic Hydrocarbons

naphthalene	2.39	7.5
acenaphthylene	1.21	35.6
acenaphthene	0.33	52.1
fluorene	0.16	16.5
phenanthrene/anthracene	0.25	21.3
fluoranthene/pyrene	0.06	31.0
chrysene/benz(a)anthracene	0.003	22.9

Table 3. PAH Dynamic Range Directly Desorbed from (0.5 g) Soil Matrix.

Compound(s)	Concentration (ng)	Signal (n=5)	Linearity (r)
Naphthalene	4000	510084 ± 22.9%	0.999
	2000	255648 ± 22.9%	
	1600	210541 ± 31.2%	
	800	110357 ± 12.9%	
	120	28371 ± 13.2%	
	80	5312 ± 23.4%	
	40	1995^a ± 22.4%	
Acenaphthylene	4000	255648 ± 22.9%	0.999
	2000	129245 ± 26.1%	
	1600	94858 ± 10.8%	
	800	51454 ± 26.1%	
	80	3575 ± 13.2%	
	40	794^a ± 17.2%	
Acenaphthene	4000	94858 ± 10.8%^{a}	0.999
	2000	23397 ± 12.7%	
	1600	20307 ± 22.9%	
	800	9936 ± 34.5%	
	80	740 ± 12.7%	
	40	251^a ± 16.8%	
Fluorene	4000	52714 ± 11.0%	0.999
	2000	24197 ± 32.8%	
	1600	18585 ± 12.7%	
	800	8971 ± 13.2%	
	120	371 ± 12.8%	
	80	794^a ± 13.4%	
	40	251^a ± 15.4%	
Phenanthrene & Anthracene	8000	42578 ± 35.4%	0.999
	4000	21245 ± 12.2%	
	3200	16271 ± 26.1%	
	1600	8084 ± 22.9%	
	240	877 ± 24.3%	
	160	3981^a ± 18.6%	
	80	316^a ± 20.2%	
Fluoranthene & Pyrene	8000	17498 ± 24.3%	0.999
	4000	8629 ± 13.8%	
	3200	6854 ± 13.8%	
	1600	3221 ± 40.1%	
	240	371 ± 12.8%	
	160	195^a ± 15.3%	

^{a}These values were not included in the dynamic range.

Table 4. Comparison of Field and Lab GC-MS Results for Total PCBs in Samples from the Resolve Superfund Site, North Dartmouth, MA

EPA ID#	Quantitative TDGC-MS (ppm)	Screening Level TDGC-MS (ppm)	Lab GC-MS (ppm)
TUF-RS-SO-A26-2-4	368.3	309.4	298.6
TUF-RS-SO-AI-5-2	274.6	213.6	260.0
TUF-RS-SO-A42-6-8	23.1	7.2	15.9
TUF-RS-SO-A37-0-2	9.1	3.2	1.3
TUF-RS-SO-AI4-0-2	7.6	1.6	5.0
TUF-RS-SO-A5A-2-4	1.7	1.7	0.4
TUF-RS-SO-NH24-2-4	1.7	-	-
TUF-RS-SO-A14-6-8	1.3	-	3.0
TUF-RS-SO-A7-4-6	ND	ND	ND

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS performed by Tufts University
Sample collected by EPA's Region 1 oversight contractor
-, Samples were not analyzed

Table 5. Comparison of Field and Lab GC-MS by Chlorination Level (ppm), Resolve Superfund site, North Dartmouth, MA.

ID Sample #	TUF-RS-SO-A15-2		TUF-RS-SO-A42-6-8	
Cl-level	Field TDGC-MS	Lab GC-MS	Field TDGC-MS	Lab GC-MS
Cl-1	12.5	ND	0.5	ND
Cl-2	7.6	10.8	1.5	1.0
Cl-3	60.3	56.5	4.5	4.1
Cl-4	121.4	122.8	5.1	5.3
Cl-5	59.5	53.6	6.3	4.3
Cl-6	20.9	15.9	3.0	1.2
Cl-7	1.7	0.4	0.3	ND
Cl-8	0.7	ND	1.9	ND
total PCB	274.6	260.0	23.1	15.9

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS (Quantitative Method) performed by Tufts University
Sample collected by EPA's Region 1 oversight contractor

Table 6. Comparison of Field and Lab GC-MS Results for PAH's From the Hocomonco Pond Superfund Site in Westborough, MA, in ppm.

	DSTB22(0'-2')		DSTB22(2'-4')	
	Lab	Field[1]	Lab	Field[1]
Naphthalene	0.1	ND	2.2	ND
Acenaphthylene	0.1	0.1	ND	0.7
Acenaphthene	1.4	0.1	6.0	0.2
Fluorene	2.9	1.5	16.3	3.0
Anthracene & Phenanthrene	8.3	40.3	81.8	72.7
Pyrene & Fluoranthene	11.8	10.6	112.2	60.5
Chrysene & Benz(a)anthracene	6.0	6.2	37.2	37.2
Benz(b)fluoranthene, Benz(k)fluoranthene, & Benz(a)pyrene	3.2	23.8	17.7	22.3

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS performed by Tufts University (Thermal Desorption of Methylene Chloride Extract)
[1] Data collected by Selected Ion Monitoring (Internal Data System)

Table 7. Comparison of Field and Lab GC-MS Results for PAH's From the Hocomonco Pond Superfund Site in Westborough, MA, in ppm.

	POND		HP-SB5	
	Lab	Field[2]	Lab	Field[1]
Naphthalene	1.3	1.9	54.8	32.0
Acenaphthylene	1.4	ND	ND	ND
Acenaphthene	0.7	ND	ND	1.2
Fluorene	2.5	ND	ND	0.8
Anthracene & Phenanthrene	16.7	10.4	ND	ND
Pyrene & Fluoranthene	30.7	43.6	ND	ND
Chrysene & Benz(a)anthracene	37.2	55.2	ND	ND

ND, compound not detected
Sample comparison on an as collected basis (i.e., soils were not dried)
Lab GC-MS performed by Lockheed ESC, Las Vegas, NV
Field GC-MS performed by Tufts University (Thermal Desorption of Methylene Chloride Extract)
[1] Data collected by Selected Ion Monitoring (Internal Data System)
[2] Data collected as Total Ion Current Chromatogram and quantified by Selected Ion Monitoring Extraction (External Data System)

DISCUSSION

ALAN CROCKETT: I found your presentation and the results extremely informative and the accuracy or the precision you were getting was fantastic. Did you say that you were using two tenths of a gram sample or a two-milligram sample?

AL ROBBAT: A half a gram.

ALAN CROCKETT: That's impressive just being able to sub-sample a jar of soil as repetitively as you've been able to. What's your preparation procedure for homogenization of soil that comes into your facility?

AL ROBBAT: These samples were all homogenized by EPA Region I. We didn't do anything more after we got them, except stir them up a little bit.

ALAN CROCKETT: How did they homogenize when you get them so homogeneous?

AL ROBBAT: Basically they screen them and then they collected them in a large jar and simply just rotated them. We did not do any of the real homogenization of the sample.

ALAN CROCKETT: What's the cost of the instrumentation by the way?

AL ROBBAT: I think it's about $180,000 but your best bet is to ask Bruckner Instruments.

JON GABRY: What are your power requirements for the unit?

AL ROBBAT: We use six 24-volt batteries. Six 24 volt batteries out in the site. We also can power-up at the site if there's electrical supply. So again, if you're interested in those types of details, I would suggest you visit the Bruckner Instruments booth.

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