CONF-9606125--2

LA-UR- 96-100

Title:

COMPARISON OF PHOTOACOUSTIC RADIOMETRY TO GAS CHROMATOGRAPHY/ MASS SPECTROMETRY METHODS FOR MONITORING CHLORINATED HYDROCARBONS

RECEIVED
MAR 13 1996
OSTI

Author(s):

Jon E. Sollid, ESA-EPE
Vincent L. Trujillo, ESA-EPE
Stephen Limback, ESA-EPE
Keith Woloshun, ESA-EPE

Submitted to:

Journal of Air and Waste Management

Los Alamos
NATIONAL LABORATORY

Form No. 836 R5
ST 2629 10/91

Comparison of Photoacoustic Radiometry to Gas Chromatography/Mass Spectrometry Methods for Monitoring Chlorinated Hydrocarbons

Jon E. Sollid
Los Alamos National Laboratory
Los Alamos, NM 87544
505-667-3672
Internet e-mail: sollid@lanl.gov

Vincent L. Trujillo, Steve P. Limback, and Keith A. Woloshun
Los Alamos National Laboratory
Los Alamos, NM 87544

INTRODUCTION

A comparison of two methods of Gas Chromatography Mass Spectrometry GCMS and a nondispersive infrared technique, PhotoAcoustic Radiometry PAR is presented in the context of field monitoring a disposal site. First is presented an historical account describing the site and early monitoring to provide an overview. The intent and nature of the monitoring program changed when it was proposed to expand the Radiological Waste Site close to the Hazardous Waste Site. Both the sampling methods and analysis techniques were refined in the course of this exercise.

The area originally included in the waste site, TA-54 at Los Alamos National Lab, is about 790 acres (320 hectares) see Figure 1. It is approximately the size of the entire DOE Fernald facility near Cincinnati, Ohio. Included in the TA-54 site are both a Hazardous Waste Site, and a Radioactive Waste Site. The Hazardous Waste Site was used for in-ground disposal from the '50s until 1985. A characterization and monitoring program was started in '88 in response to EPA requirements. A permit is now required in order legally to operate the sites. As part of the condition of the permit a monitoring program is required. Twenty-seven monitoring wells were drilled. The disposal shafts are generally no more than 85'. The monitoring wells are as deep as 300', with from 3 to 12 sampling ports. There are a total of 173 ports to sample a volume of 383 million cubic yards (292 million cubic meters).

The first sampling technique used was to purge one headspace (the volume of gas in the tubing leading from the sampler to the underground port) and pass 1.2 liters of gas thru commercially prepared ampules of granulated activated coconut charcoal. The analyte was removed from the charcoal by a solvent, carbon disulfide, which was then processed by GCMS. The concentration of 12 volatile organics were measure in this way. The analytes are listed, marked by and asterisk (*), in Table 1.

This was adequate to satisfy the requirements of the permit until the early '90s when plans were made to expand the Radiological Waste Site. In order to provide more space for Radioactive Waste, and to avoid the creation of Mixed Waste, retraction of the Volatile Organic Compounds VOC plume was required. To engineer a retraction, or remediation scheme, better data were required for the much smaller area surround the primary Hazardous Waste Site.

DEVELOPMENT OF THERMAL DESORPTION GCMS (TDGCMS)

To reduce the effects of transients in the early part of the gas flow a larger volume was purged. Previously one headspace was used. For TDGCMS 5 headspaces were purged. To increase the range over which concentration measurements could be made, and to provide redundancy as a quality check, the gas flow was split into two sorbent tubes. One receives ten times more gas than the other. The sorbent tubes are more complex. They are not simple ampules of granulated activated charcoal, but have 3 components. There are two different grades of carbotrap™ and a layer of carbosieve™ available from Supelco. Care must be given to the temperature schedule during desorption to avoid inducing breakdown reactions in the analytes to be measured. After a period of development the TDGCMS method[1] worked quite well. However two samples are taken per port. Also TDGCMS is sensitive to 50 analytes, hydrocarbons and chlorocarbons plus 2 chlorofluorocharbons, not just 12 as previously. The analytes are listed in Table 1. All of the 12 compounds previously measured by carbon disulfide solvent extraction are also measured by the thermal desorption method.

Using TDGCMS the analysis cost increased. Also there is a significant delay (months) in obtaining results from both methods of GCMS. A large portion of the delay is attributable to the "chain-of-custody" requirements.

SELECTION OF PHOTOACOUSTIC RADIOMETRY

An instrument that could give results in the field, or at least the same day, was needed. The site was well characterized. Speciation was not required. The compounds present are known with fair confidence. It was thought that the physical extent and motion of the plume could be adequately tracked by monitoring a few of the most dominant analytes.

For indoor air quality monitoring often only a few compounds are present. PhotoAcoustic Radiometers, such as the Brüel og Kjær Model 1302 Multigas Analyzer, are used for this purpose. To validate the concept bench tests were done[2]. Satisfied that the concept was sound, one PAR instrument was adapted for field use[3] at the Hazardous Waste Site by mounting it in the back of a pickup truck along with the purge pump and TDGCMS sampling unit.

PhotoAcoustic Radiometry PAR is a nondispersive infrared technique. Narrow band filters in the 2-15 μm region of the spectrum allow an incandescent source to illuminate the soil pore-gas sample, exciting resonances in the vibrational and rotational bands of the molecules. The excitation relaxes to translational energy, becoming a pressure pulse, which is detected with sensitive microphones. Figure 2 is a conceptual illustration of the principle of operation of the PAR.

Provided the compounds of greatest interest are not too similar PAR will work well. If the spectra of the compounds of interest are too similar it is impossible to distinguish one from the other. That is, both compounds can absorb light that passes thru the same narrow band filter. The compounds are said to interfere with each other. The presence of an unsuspected interfering compound causes over estimation of the concentration of the compound for which the measurement is made. In the first tests concentrations of the principal analytes were overestimated by the PAR by as much as a factor of five in comparison to TDGCMS measurements. As TDGCMS technique improved the ratios for TCAand TCE were on the order of a factor of two, cf. the discussion below. Measurements for PCE were never better than an order of magnitude.

When it was realized that in addition to hydrocarbons and chlorocarbons there were abundant chlorofluorocarbons the filters were changed to correspond to the most abundant compounds, TCA, R11, R113, and TCE, in descending order.

BENCH TEST RESULTS OF THE PAR[2]

Using single calibration gases mixed in dry nitrogen accuracy of 5% or better and precision or reproducibility of 0.5% are easy to obtain. A problem with drift was encountered, amounting to -7% per hour for repeated, continuous measurement. A measurement takes on the order of minutes. Generally the first measurement is right on. During a measurement cycle 225 ml of gas is pumped into the sample cell and irradiated sequentially by infrared which passes thru six separate filters. One filter must be for water vapor. Five are of the user's choice. In principle a single filter could be used for up to 5 different gases. In practice it is better to stick to one gas per filter.

FIELD TEST COMPARISONS PAR TO TDGCMS

To illustrate performance in the field Table 2 shows four sets of sequential quarterly TDGCMS concentration measurements, and five sets of PAR concentration measurements on soil pore-gas from the same well. The top(bottom) part of the table lists the twenty compounds measured in this well, their CAS numbers, molecular weights, and the concentration found by TDGCMS(PAR). For the TDGCMS data there are two columns for each quarter. The column with an odd(even) sample number corresponds to the sorbent tube that received 509(51)ml of soil pore-gas. The first(last) two quarters of data were taken from the port at 82(18) feet. In both cases these were the depths that produced the highest TCA concentrations according to the PAR. If the TDGCMS data were entirely consistent the values in both columns, for a given quarter, would be identical. The fact that they are not is sometimes attributable to the measurements being at the extremes of their ranges. On the high end the sorbent tube may have saturated, or "broken thru." On the low end the sorbent had values near the limit of quantization.

The ratio of the concentration as measured by the high volume tube to the concentration as measured by the low volume tube is an indication of how well the analyses and sampling were done. The closer the number is to one, the better the agreement between high and low volume tubes, as shown in Table 3. Note that the analyses improved as time progressed. In the second, third, quarter '94 and first quarter of '95 the average ratios were 3.26, 0.58, 0.93 with average deviations of 3.06, 0.38, and 0.24. The measurements of the odd samples for the fourth quarter '94 were lost due to a computer problem. The worst agreement is for the most prevalent analyte 1,1,1-trichloroethane or TCA The reason being that the large volume sample "breaks thru" or saturates, hence it gives at best a lower limit to the maximum value. In those cases the measurement from the low volume tube is likely the most accurate.

Consider the comparison of the PAR data to the TDGCMS data. Examine the ratio of the PAR measured concentrations to the TDGCMS measurements

	PAR/TDGCMS			
	2Q94	3Q94	4Q94	1Q95
TCA	5.06	2.36	2.10	4.19
TCE	4.38	2.57	1.78	5.95
PCE	18.45	15.62	9.23	
R11				0.65
R113				2.07

Perfect agreement would result in all ones above. Probably as a result of better TDGCMS technique the ratios improve for all measured analytes over the second, third and fourth quarters of '94 culminating in the best ratios: 1.78 for TCE and 2.10 for TCA. PCE was always over estimated by at least 9.23. In the first quarter of '95 the filters in the PAR were changed to measure the freon, listed in the table as refrigerants R11 and R113, since it was determined that in this area of the plume chlorofluorocarbons were prevalent. Unfortunately the measurements for TCA and TCE deteriorated, ratios were 4.19 and 5.95 respectively, though the measurements for the freons were quite good R11(0.65) and R113(2.07). Well 54-2015 was not one of those sampled the second quarter of '95. Results from later quarters are not available either since the TDGCMS sampling unit was damaged in a hail storm and remains to be repaired or replaced. Contrary to expectations, correspondence between PAR and TDGCMS measurements did not improve for the most abundant compounds when the PAR was reconfigured, although measurements of the dominant freons were reasonably good.

Comparisons in later quarters will be suspect since the sampling technique reverted to a single sorption tube and an estimated volume based on a positive displacement measurement rather that a true mass flow.

REDUCING SAMPLING EFFECTS

The field comparison, given above, for the TDGCMS and PAR methods, incorporates all the difficulties of the sampling methods, and long term comparability.[34] There are questions about hold time, temperature history, pressure history, humidity, moisture effects, and plumbing integrity, that effect the analysis. These raise questions about sample validity. Were all the samples taken in identical fashion? Was the plumbing leak free? What was the ambient temperature? There is evidence that when the ambient surface temperature is below dew point condensate in the tubing skews the measurements., And at much lower temperatures the condensate will freeze and block the tube. In an effort to isolate sampling effects some samples were taken in Tedlar® bags and analyzed directly by both TDGCMS and PAR. The soil pore-gas in the Tedlar® bags was withdrawn by syringe thru a rubber septum and injected, in a controlled, uniform way, onto trap material in the lab to start the TDGCMS procedure. A similar sample was drawn and analyzed by PAR. This was done on two separate wells at approximately the same distance from the expected contamination source. One well, 2024, showed significantly more contamination than the other, 2023, at all depths. Table 4 shows statistical measures of concentration for all analytes above quantization limit for both wells, by both techniques. For well 2023 there were only 3 measurements by TDGCMS and one measurement via PAR. For well 2024, however, there were 5 measurements by each method. In the table are listed the average concentration for each analyte in ppm by volume; the average deviation; and the ratio of the average deviation to the average. The ratio of the average deviation to the average value gives an indication of the repeatability of the measurement. For well 2023(2024) the mean of the ratios of the average deviation to the average value was 0.33(0.34) by TDGCMS. For well 2024 the mean of the ratios of the average deviation to the average value was 0.15 by PAR. So the measurements were relatively similar from well to well by technique, and roughly twice as precise using PAR compared to TDGCMS. Was the constellation of analytes similar from well to well? Consider the concentration of analytes normalized to the TCA value for each well by each technique, as shown below

Concentrations, by technique, normalized to TCA

	TDGCMS		PAR	
Well Number	2023	2024	2023	2024
Analyte				
R11	...	0.05	0.03	0.02
R113	0.02	0.25	0.24	0.25
TCA	1.00	1.00	1.00	1.00
TCE	0.47	0.22	0.25	0.23

The only inconsistent number is for TCE at well 2023 measured via TDGCMS. At 0.47 there seems to be about twice more TCE than anticipated by the other TDGCMS measurement, and by PAR. This appeared to be a good measurement from the small average deviation. However the close agreement might be a small sample fluke. Or it may be an indication of a anisotropy in the ground. Perhaps the TCE tends more to flow toward well 2023. The PAR and TDGCMS distributions are quite similar. So if there are interference effects they seem to be uniform from compound to compound.

Consider next the ratios of the concentration measured by PAR to those measured by TDGCMS, as shown below

Concentration ratios PAR/TDGCMS

Well Number Analyte	2023	2024
R11		0.925
R113	3.260	2.270
TCA	2.754	2.311
TCE	1.476	2.411
mean	2.497	1.979

The values range from 0.93 to 3.26 with the average for the least polluted well, 2023, being about 2.5, while the average for the well with higher concentration, 2024, being about 2.0. Note, these measurements were made during the third quarter of '95 with the same filters in place as during the first quarter of '95. In the interim the PAR was recalibrated, which may account for the better performance than was demonstrated in the first quarter '95. It may also demonstrate the difficulty of proper sampling when the ambient temperature is less than dew point, as was the case for most of the first quarter '95 measurements.

UTILITY OF THE PAR FOR PILOT EXTRACTION TEST

The pilot extraction program used PAR data extensively and exclusively to determine the effect of a very large scale active vapor extraction. A complete description of the pilot extraction test results is available[5] and will not be repeated here. Suffice it to say it would not have been possible to access the effects of the active extraction without the use of the PAR.

To do the before and after concentration surveys two PAR units were used. One, shown in Figure 2 was the roving unit. Its use provided a large scale collection of data with long term collection times (days and weeks). An automated unit was built by SEA, Inc. that automatically sampled up to 16 ports every 3 hours. The unit was described elsewhere.[6] Its use on this pilot extraction program was presented in more detail earlier.[7] Without the capability of reliable, same-day measurement the results for the pilot extraction test would still be pending. The feasibility of active vapor extraction was established and a tentative design is proposed.

UNRESOLVED DIFFICULTIES AND CAVEATS

In the course of the pilot extraction test both PARs were fitted with optical filters with the same specifications (i.e. they had the same manufacturer's part numbers). They were calibrated, by the factory, using single gases with the balance in dry nitrogen, and using a mixture with all five analytes present. The results measuring the mixture for both units, one identified as the "V-unit" and the other as the "R-unit," are shown in Table 5. The maximum error occurs with TCE and by as much as 14%. Both units err on the high side for TCE, but agree with each other within 3%. The mean error for both units for all analytes is about 3%. Interunit comparisons were made in the field on two wells. For one well the agreement was within 5%. However, on the other well the difference between units for a single analyte was on the order of 20%. Possibly the mix of gases in that particular well was such to cause the large discrepancy. Consequently in looking for changes, the same unit was always used on the same ports and interunit comparisons were not used.

As is known in water sampling, plastics can absorb some of the contaminants. Up to 30% absorption in soft Tygon® was discovered while doing gas phase sampling on tubing runs up to 80 feet. Hence during the pilot extraction test all Tygon® was removed and replaced by Teflon® lined Tygon® tubing.

SUMMARY

To summarize, PAR and TDGCMS are complementary techniques. Use GCMS techniques to do the initial survey to identify the dominant compounds, after which the plume motion and extent can be effectively monitored at much lower cost using PAR. For the LANL Hazardous Waste Site this lead to a cost saving of more than $500,000 per year. This represents the difference in cost between analyzing 454 TCGCMS samples per quarter, as was previously required, at a cost of $300 per sample, and 28 samples per quarter as is currently required. This is only the savings in GCMS analysis cost. It does not reflect the increase in cost required to do the PAR sampling. The PAR direct cost is less than $100,000 per year, including the cost of the PAR. Not only is PAR cost effective, but timely, repeatable results are obtained.

REFERENCES

1. A.J. Lombardo, C.P. Leibman and J.E. Sollid, "Field Monitoring of Volatile Organic Compounds via Photoacoustic Radiometry (PAR) and Thermal Desorption Gas Chromatography/Mass Spectrometry (TDGCMS) II: TDGCMS Development," Proceedings of the Eighth Technology Information Exchange sponsored by The U.S. Dept of Energy, Santa Fe, New Mexico, April 16 - 18, 1996, to be presented.
2. J.E. Sollid, V.L. Trujillo, S.P. Limback, "Field Monitoring of Volatile Organic Compounds via Photoacoustic Radiometry (PAR) and Thermal Desorption Gas Chromatography/Mass Spectrometry (TDGCMS) I: PAR Development," ibid. 1.
3. J.E. Sollid, "Soil Pore-Gas Sampling by Photoacoustic Radiometry,"Proceedings of The Optical Instrumentation for Gas Emissions Monitoring and Atmospheric Measurements Conference," Cosponsored by the Air & Waste Management Association, Pittsburgh, PA and The International Society for Optical Engineering

(the SPIE), Bellingham, WA. The conference was held in McLean, VA, 7-10 Nov. 1994. The Proceedings were published as SPIE Proc. Vol 2366, p.12.
4. J.E. Sollid and K. Woloshun, "Field Monitoring of Volatile Organic Compounds via Photoacoustic Radiometry (PAR) and Thermal Desorption Gas Chromatography/Mass Spectrometry (TDGCMS) III: Sampling Lessons," ibid. 1.
5. K. Woloshun, Pilot Extraction Test Results for TA-54, LA-UR TBI, Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87544, 1996, 20pp.
6. P. Zakian, "Automated Soil Gas Monitoring with MultiScan® - A Stand-Alone, Real-Time, Multi-Point Soil Gas Sampling and Analysis System," Proceedings of ER '95 Technical Conference, Denver, CO, 11-13 Sept. 1995.
7. W. Lowry, P. Zakian, K. Woloshun, and R. Gilkeson, "Real Time Monitoring of Soil Gas Contaminants During a Very Large Scale Vapor Extraction Test," ibid. 1.

Table 1 Thermal Desorption Analytes
Table 2 Quarterly concentration measurements by TDGCMS/PAR
Table 3 Ratio of Concentrations by high volume tubes to low volume tubes
Table 4 Concentrations Measurements ~~[ppm]~~ for Wells 2023,4 by TDGCMS & PAR
Table 5 Calibration results for both PARs on mixed gases

Figure 1 Map of Los Alamos National Lab showing the Waste Site, TA-54.
Figure 2 Conceptual sketch of PAR

Table 1. Thermal Desorption Analytes

	COMPOUND	CAS#
1	1,1,1,2-Tetrachloroethane	630206
2	1,1,1-Trichloroethane *	71556
3	1,1,2,2-Tetrachloroethane	79345
4	1,1,2-Trichloroethane	79005
5	1,1-Dichloroethane	75343
6	1,1-Dichloroethene	75354
7	1,1-Dichloropropene	563586
8	1,2,4-Trimethylbenzene *	95636
9	1,2-Dichlorobenzene	95501
10	1,2-Dichloroethane	107062
11	1,2-Dichloropropane	78875
12	1,3,5-Trimethylbenzene	108678
13	1,3-Dichlorobenzene	541731
14	1,4-Dichlorobenzene	106467
15	2-Butanone	78933
16	2-Hexanone	591786
17	4-Methyl-2-pentanone	108101
18	Acetone	67641
19	Benzene *	71432
20	Bromobenzene *	108861
21	Bromodichloromethane	75274
22	Bromoform	75252
23	Bromomchloromethane	74975
24	Bromomethane	74839
25	c-1,2-Dichloroethene	156592
26	c-1,3-Dichloropropene	10061015
27	Carbon Disulfide	75150
28	Carbon Tetrachloride *	56235
29	Chlorobenzene *	108907
30	Chlorodibromomethane	124481
31	Chloroethane	75003
32	Chloroform *	67663
33	Chloromethane	74873
34	Dibromomethane	74953
35	Dichlorodifluoromethane	75718
36	Ethylbenzene *	100414
37	Methylene Chloride	75092
38	n-Propylbenzene	103651
39	o,m,p-Xylene (mixed) *	1330207
40	Styrene	100425
41	t-1,2-dichloroethene	156605
42	t-1,3-Dichloropropene	10061026
43	Tetrachloroethene *	127184
44	Toluene *	108883
45	Trichloroethene *	79016
46	Trichlorofluoromethane	75694
47	Trichlorotrifluoroethane	76131
48	Vinyl Chloride	75014
	Chlorofluorocarbons	
	tricholorfluromethane R-11	75-69-4
	tricholotrifluoretheneR-113	76-13-1

Compounds marked * were measured by solvent desorption

Table 2. Quarterly concentration measurements by TDGCMS PAR

TDGCMS			2Q94	2Q94	3Q94	3Q94	4Q94	4Q94	1Q95	1Q95
COMPOUND	CAS #	MOL WT	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)
Dichlorodifluoromethane	75718	121		1	2	2			1	1
Trichlorofluoromethane	75694	137	5	4	8	257		131	28	36
1,1-Dichloroethene	75354	95	40	8	8	29		34	9	11
Acetone	67641	58		1	1	5			1	2
Trichlorotrifluoroethane	76131	187	58	4	11	82		75	31	61
Methylene Chloride	75092	85	90	69	173	118		76	23	18
1,1-Dichloroethane	75343	97	4	5	7	10		7	3	3
Chloroform	67663	119	6	8	12	15		12	3	2
1,1,1-Trichloroethane	71556	133	265	35	132	551		419	60	132
Carbon Tetrachloride	56235	154				2			1	1
1,2-Dichloroethane	107062	97	8	7	13	17		16	1	1
Benzene	71432	78		2	2	4				
1,2-Dichloropropane	78875	113	17	9	17	23		17	4	4
Trichloroethene	79016	131	67	38	108	114		119	7	6
Dibromomethane	74953	174				2				
Toluene	108883	92	11	11	17	13		11		
Tetrachloroethene	127184	166	7	7	8	6		9	1	1
Chlorobenzene	108907	113		1		3				
Ethylbenzene	100414	106		1		3				
o,m,p-Xylene (mixed)	1330207	106		3	2	3				
			2Q94	2Q94	3Q94	3Q94	4Q94	4Q94	1Q95	1Q95
PAR										
COMPOUND	CAS #	MOL WT	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)	ppm(vol)
Dichlorodifluoromethane	75718	121								
Trichlorofluoromethane	75694	137							18	18
1,1-Dichloroethene	75354	95								
Acetone	67641	58								
Trichlorotrifluoroethane	76131	187							127	127
Methylene Chloride	75092	85								
1,1-Dichloroethane	75343	97								
Chloroform	67663	119								
1,1,1-Trichloroethane	71556	133	1340	1340	1170	1300	880	880	554	554
Carbon Tetrachloride	56235	154								
1,2-Dichloroethane	107062	97								
Benzene	71432	78								
1,2-Dichloropropane	78875	113								
Trichloroethene	79016	131	294	294	276	296	211	211	40	40
Dibromomethane	74953	174								
Toluene	108883	92								
Tetrachloroethene	127184	166	131	131	122	136	87	87		
Chlorobenzene	108907	113								
Ethylbenzene	100414	106								
o,m,p-Xylene (mixed)	1330207	106								
			2Q94	2Q94	3Q94	3Q94	4Q94	4Q94	1Q95	1Q95

Table 3. Ratio of concentrations measured by high volume tubes to low volume tubes

COMPOUND	CAS #	2Q94	3Q94	1Q95
Dichlorodifluoromethane	75718		0.65	1.25
Trichlorofluoromethane	75694	1.33	0.03	0.76
1,1-Dichloroethene	75354	5.20	0.27	0.88
Acetone	67641		0.24	0.50
Trichlorotrifluoroethane	76131	15.42	0.13	0.51
Methylene Chloride	75092	1.30	1.47	1.27
1,1-Dichloroethane	75343	0.72	0.72	1.10
Chloroform	67663	0.81	0.83	1.20
1,1,1-Trichloroethane	71556	7.50	0.24	0.45
Carbon Tetrachloride	56235		0.15	0.80
1,2-Dichloroethane	107062	1.13	0.80	1.00
Benzene	71432		0.69	
1,2-Dichloropropane	78875	2.00	0.76	1.00
Trichloroethene	79016	1.76	0.94	1.11
Dibromomethane	74953		0.10	
Toluene	108883	0.97	1.26	
Tetrachloroethene	127184	1.00	1.26	1.14
Chlorobenzene	108907		0.16	
Ethylbenzene	100414		0.14	
o,m,p-Xylene (mixed)	1330207		0.74	
	average	3.26	0.58	0.93
	avedev	3.06	0.38	0.24
	stdev	4.35	0.44	0.28

Table 4. Concentration Measurements [ppm] for Wells 2023,4 by TDGCMS and PAR

		TDGCMS			**TDGCMS**	
		2023-120'			**2024-160'**	
	ave	**ave dev**	**ave dev/ave**	**ave**	**ave dev**	**ave dev/ave**
R11				1.46	0.46	0.32
1,1,-dichloroethane				2.73	1.31	0.48
R113	1.81	0.86	0.48	7.70	2.01	0.26
methyl chloride				4.37	1.14	0.26
chloroform				1.48	0.33	0.22
TCA	9.04	3.09	0.34	30.62	8.15	0.27
TCE	4.26	0.67	0.16	6.81	4.05	0.54
mean			**0.33**			**0.34**

		PAR			**PAR**	
		2023-120'			**2024-160'**	
	ave	**ave dev**	**ave dev/ave**	**ave**	**ave dev**	**ave dev/ave**
R11	0.70			1.35	0.46	0.34
1,1,-dichloroethane						
R113	5.90			17.48	1.26	0.07
methyl chloride						
chloroform						
TCA	24.90			70.76	4.54	0.06
TCE	6.30			16.42	1.75	0.11
mean						**0.15**

Table 5. Calibration Results for both PAR units on mixed gases.

		Concentration [ppm]	
Analytes	Mix	Unit R	Unit V
TCA	22.4	21.6	22.30
TCE	112	99.1	96.40
R11	64.1	64.1	68.90
R113	66.6	67.8	67.10
Carbon Dioxide	184	178	171.00
		deviation	deviation
TCA		0.8	0.1
TCE		12.9	15.6
R11		0	-4.8
R113		-1.2	-0.5
Carbon Dioxide		6	13
		%	%
TCA		3.57	0.45
TCE		11.52	13.93
R11		0.00	-7.49
R113		-1.80	-0.75
Carbon Dioxide		3.26	7.07
	mean	**3.31**	**2.64**

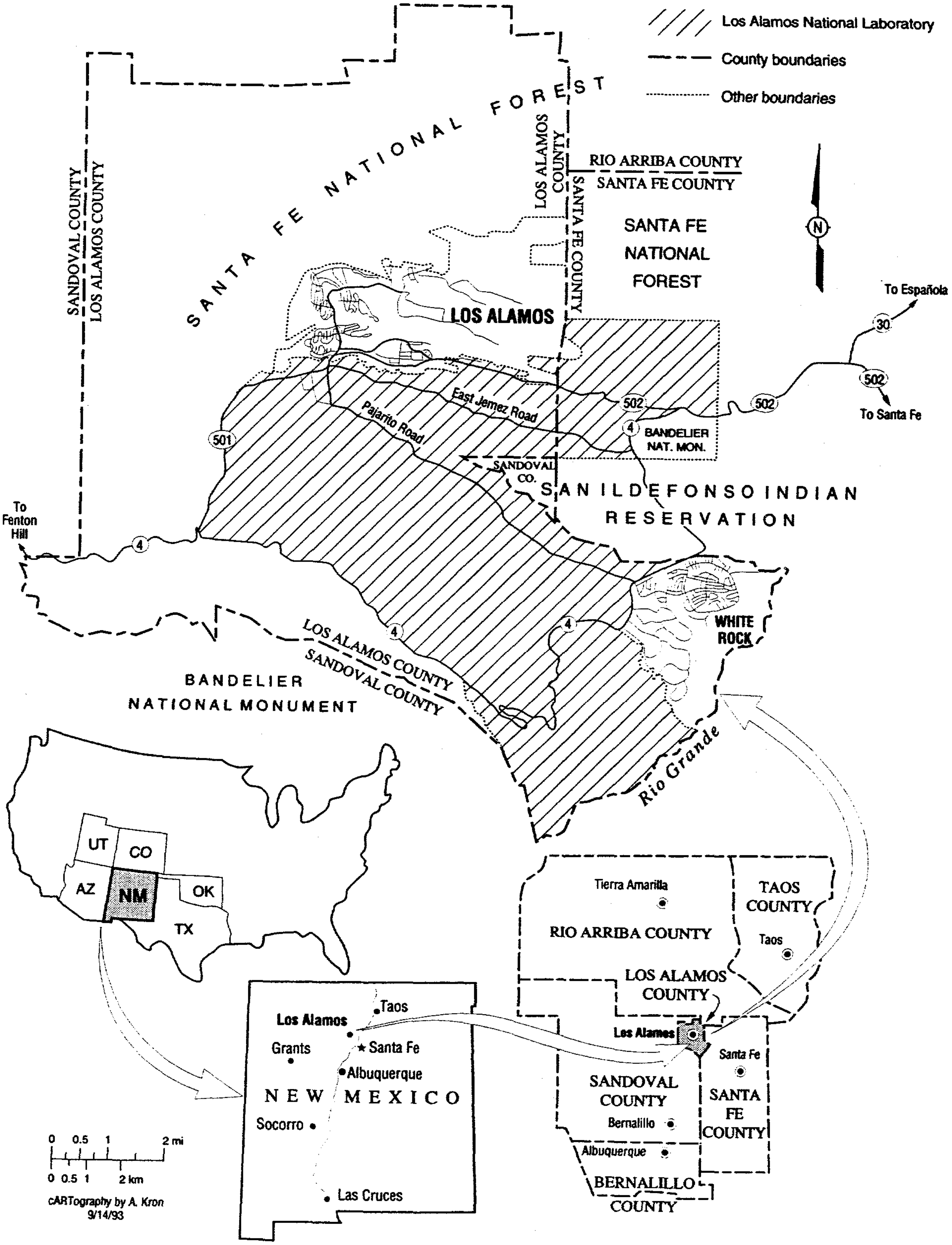

FIGURE 1

MAP OF LOS ALAMOS NATIONAL LABORATORY SHOWING THE WASTE SITE, TA-54

Measurement System of the Multigas Monitor Type 1302

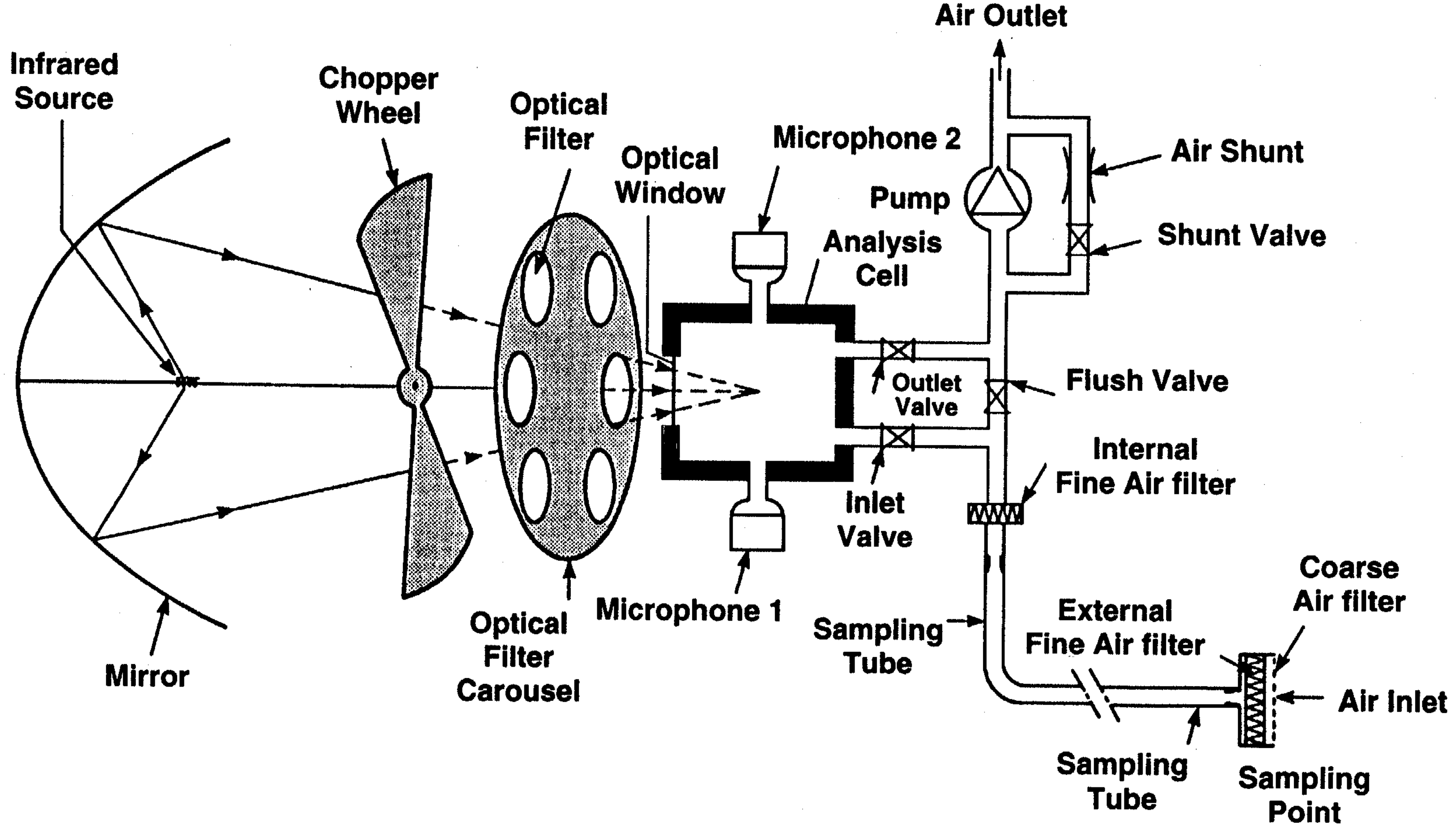

Figure 2

CONCEPTUAL DIAGRAM OF THE PAR