

Joint Quality Management and Quality Assurance Project Plan

Drum Sampler Demonstration of PM Mass and XRF Elements

U.S. Environmental Protection Agency
Office of Research and Development
National Center for Environmental Assessment

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Approvals for Project Team

Approvals for EPA

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1. Project Organization and Responsibilities of Principal Investigator(s)

The DELTA (Detection and Evaluation of Long-range Transport of Aerosols) group is a small organization associated with the University of California, Davis. The Director, Dr. Thomas Cahill, is responsible for all Quality Assurance activities.

2. Problem Definition and Background

PM2.5 speciation sampling (determination of a suite of elements measured by X-ray fluorescence, called XRF-elements) is currently conducted once every sixth day (once every third day at a few monitoring sites). Everyday data is needed to provide more accurate and reliable epidemiological analyses and to obtain information sooner. However, costs using the current system are prohibitive. A new technique, developed at the University of California, Davis, CA, called the Drum Sampler with Synchrotron-XRF analysis for XRF-elements, offers everyday speciation data at a cost comparable to one day in three using the current system. The Drum Sampler provides information on PM10-2.5 and ultrafine PM as well as PM2.5 and with increased time and particle size information. EPA would like to evaluate the Drum Sampler as a possible alternate to the current filter-based monitoring system with anode-generated X-rays for XRF analysis (A-XRF).

EPA wishes to determine 1) if the drum sampler can operate effectively and with minimum care at a state agency monitoring site, 2) if the additional data obtained (five size ranges instead of one, four time intervals a day instead of one) will make it possible, using source apportionment modeling, to identify more source categories and to obtain more accurate and reliable information on the contribution of each source category to the particle mass, and 3) to determine how well the Drum Sampler data agrees with the data obtained from the current speciation sampling system. Under this procurement the contractor shall to provide a Drum Sampler for use at a state agency monitoring site for 4-6 weeks and analyze the collected particles. The University of California, Davis is currently the only organization that offers Drum Samplers with Synchrotron-XRF analysis for XRF-elements.

3. Project Description, Documentation, and Records

Project Description

Thomas Cahill, Principal Investigator, will supply a Drum Sampler; transport it to a state agency monitoring site in New York State where state personnel will operate the Sampler and transport the Sampler back to the DELTA group; analyze the collected samples for particle mass concentration by beta gauge, black carbon by optical measurements, and elemental concentrations by Synchrotron-XRF for four time periods a day and in 5 size ranges (including after-filter size range) for 25 or more days; and provide the data to EPA in a Data Report.

Documentation

Documentation is given in the attached Data Quality Assurance Plan as follows:

Impaction.....Article I&III p.1-2,5-6
Drum Samplers including DELTA Drum-5,
to be used in this study.....Section 4.02 p.7-8

Elements by Synchrotron XRF.....	Section 4.03	p.9-13
Mass by Beta gauge.....	Section 4.06	p.17
Black Carbon by Optical Extinction.....	Section 4.07	p.17-20
Validation.....	Article V	p.23-45
Flow.....	Section 5.01	p.23
Cutpoint.....	Section 5.02	p.23
Sample Collection.....	Section 5.03	p.23
Time Resolution.....	Section 5.04	p.23-27
Filter Comparisons.....	Section 6.01	p.29-39
Drum to Filter Comparisons.....	Section 6.02	p.39-45
SOP for Sample Collection.....	Appendix A	
SOP for S-XRF Analysis.....	Appendix B	

Quantitative or qualitative measures by which the success of the project or task will be determined, such as the final use of the data;

- b. Sample selection, collection and preparation;
Samples will be collected at a state monitoring site in New York City as specified by the EPA Project Officer.
- c. Sample handling and custody requirements;
While in New York City the sampler and samples will be in the custody of Dirk Felton, New York State Department of Environmental Conservation; otherwise the sampler and samples will be in the custody of Thomas Cahill.
- d. Measurement methods and performance characteristics;
Measurement methods include S-XRF for XRF elements, beta gauge for mass, and optical extinction for black carbon.
- e. Standard QA procedures or alternatives;
Standard QA procedures will be followed as described in the attached DELTA Group Data Quality Assurance Plan.
- f. Data reduction and reporting procedures;
Concentration will be derived from flow rates and concentrations measured per cm² of impactor or filter surface. Data will be reported to EPA in electronic spread sheet format.
- g. and, Plans for review of the project during operation oversight).
The Principal Investigator will inform the Project Officer of any problems that arise during the study and together they will devise a plan to deal with such problems. In addition, Dirk Felton will inform the EPA Project Officer of any problems that occur during operation of the Drum Sampler in New York City and the Project Officer will arrange with, Dirk Felton, and Thomas Cahill to deal with such problems.

5. Data Quality Objectives (DQOs), including an explanation of data use and acceptance criteria (precision, accuracy, representativeness, completeness, and comparability) as agreed to by the customer for the data.

The purpose of this contract is to evaluate the suitability of the Drum Sampler with S-XRF analyses of elements, beta gauge measurements of mass, and optical extinction measurements of black carbon as an alternate to the current speciation monitoring system using filters and A-XRF. The contractor shall provide a sampler and perform the analyses according to his normal procedures and supply concentration data to EPA. EPA will then evaluate the results and compare them to results from a collocated speciation monitor using the current filter and A-XRF technique. Key questions of concern to EPA and that will be used to judge the success of the contract are:

1. Simplicity of operation. Can the Drum Sampler be successfully operated at a state-monitoring site by state employees assigned to operate such sites? How does the operator time required compare to that of the current system?
2. Data completeness. How does the % of possible samples analyzed compare to that obtained with the current system?
3. Sensitivity. How does the % of measurements above the level of detection (LOD) compare with the current system? Does the S-XRF technique provide measurements, above the LOD, for more elements than the current system?
4. Comparability. How well do the measurements with the Drum Sampler, S-XRF system compare to those obtained with the current system?
5. Ultra fine particle measurements. Did the "streaker" addition to the Drum impactor operate efficiently? Was there sufficient material on the "streaker" after-filter to permit successful quantification?
6. Source category apportionment. Does the additional size and time resolution, compared to the current system, identify more source categories and/or provide better source category signatures?

6. Reconciliation with Data Quality Objectives (describes how issues which come up during the project that required adjustment to the DQOs will be resolved with the customer for the data).

The contractor shall inform the project officer of any issues that would interfere with the normal operation of the sampler and analysis of the samples. Any issues involving Data Quality Objectives will be resolved by discussions with the Project Officer (and if necessary the Contracting Officer and the Quality Assurance Officer).

Appendix A

DRUM Quality Assurance Protocols

DELTA* Group DRUM samplers

Original Version 8/02. (DQAP 8/02)

Current version January, 2008 (DQAP 1/08)

Tom Cahill and DELTA* Group staff

Dr. Steve S. Cliff, Prof. Kevin D. Perry (Meteorology, U. Utah), Dr. David E. Barnes, Lee Portnoff (DRUMAir)

*Detection and Evaluation of Long-range Transport of Aerosols

Newest information

A. Summary comparison, all DELTA S-XRF double blind experiments

Below we summarize all DELTA Group S-XRF inter-comparisons in the past 5 years. Note that there were problems with the ARB RAAS analyses since the two internal ARB X-RF to ARB RAAS comparisons agreed only at the level 1.29 ± 0.63 for all co-measured elements. (DQAP v. 8.02, pg 32) We also give averages below without the

ARB RAAS data. A comparison was also done with IMPROVE in the Yosemite study (2002) but this comparison is not included since IMPROVE has also since identified serious deficiencies in data from that period (White et al, AAAR 2004)

Study and date	Methods	Average ratio, Al to Fe	Std. dev.	Average ratio, Cu to Pb	Std. dev.
BRAVO, 1999	PIXE vs S-XRF	0.99	0.04		
BRAVO, 1999	CNL XRF vs S-XRF			1.24	0.14
FACES, 2001	ARB XRF vs S-XRF	0.93	0.21	1.02	0.08
FACES, 2001	ARB RAAS vs S-XRF	(0.98)	0.27	(0.74)	0.23
ARB LTAD 2005	DRI XRF vs S-XRF	1.037	0.085	0.907	0.009
All prior studies	Average (no RAAS)	0.984 (0.985)	0.15 (0.11)	0.977 (1.055)	0.115 (0.076)

B. DELTA Group S-XRF versus DRI XRF, ARB Lake Tahoe Atmospheric Deposition (LTAD) study, (2005)

This comparison for silicon in very lightly loaded samples (a few $\mu\text{g}/\text{m}^3$), was typical of major elements. For many minor elements, S-XRF had much higher sensitivities and MDL limitations with the DRI data made comparisons impossible. Specifically, the very important element for lake clarity, phosphorus, was seen above MDL in only about 1% of analyses by DRI, while phosphorus was seen in over 80% of DELTA Group S-XRF analyses. All these data are in the comparison table (above)

Silicon

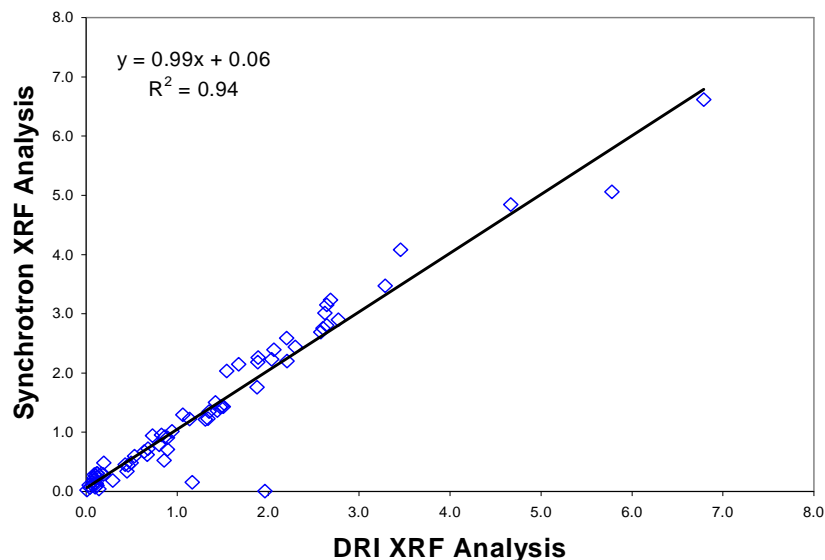


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Article I. Introduction

Impaction is the process in which particles are stripped from an air stream by forcing the gasses to make a sharp bend. Particles above a certain size possess so much momentum that they can not follow the air stream and strike a collection surface which is available for later analysis of mass and composition. Removal of particles from an air-stream by impaction followed by mass and compositional analysis has always been an alternative to filter sampling, yet has been little utilized for routine analysis because of lack of suitable analytical techniques.

The most obvious and important advantage of impaction, as opposed to filtration, is that two key aerosol parameters, size and composition, can be simultaneously established.

There are many advantages of impaction as a sampling method:

- For two of the most common configurations, an orifice and an infinite slot, theoretical predictions can be made and empirically verified that give the cut point and shape of the collection efficiency of an impaction stage.
- The air stream moves over the sample, not through it as in filtration, reducing desiccation and chemical transformations of the collected sample.
- Almost complete control of the type of surface on which the particles are impacted, as opposed to the limited choice of filter types
- By varying the speed of the air stream and the sharpness of the bend, one can separate particles into numerous size classifications while retaining a sample for analysis.

There are also several disadvantages to impaction as a sampling method:

- Only a limited amount of material is available for mass and compositional analysis, as one can not collect more than a few mono-layers of particles before particle bounce and mis-sizing are a potential problem.
- Impactors are operationally complex, with key parameters that must be maintained by either maintenance or instrumentation.
- Because impactors are not widely used, there is a lack of quality assurance experience.
- Because impactors are not widely used, there are few people or groups expert in their application.
- Interpretation of impactor data is often complex.
- Costs of analysis can be high.

As an example of this last problem, consider the case of a 8 stage impactor. For all else being equal, there are 8 times as many samples to analyze as a single 24 hr filter. But the problem is compounded by the fact that each sample has on average only 1/8 as much mass as the filter, thus further raising the cost of analysis or decreasing the number of species that can be detected. For time resolved samplers, such as the DRUM, typically 4 to 8 samples are collected per 24 hour period, yielding 32 to 64 samples to analyze as opposed to a single 24 hr filter.

It has been the consistent effort of the Air Quality Group and DELTA Group at UC Davis to minimize the disadvantages of impaction and maximize the benefits of impaction as a routine tool for aerosol analysis. Key to this effort are solid and well documented quality assurance protocols and reduction of analytical costs per unit of information.

Article II. Quality Assurance - General Concepts

Section 2.01 Overall goals of QA/QC protocols

Level 0

Level 0 QA refers to all those operations necessary to insure that the data are accurate and precise. Standards and procedures are included in Level 0 validation.

Level 1

Level 1 QA refers to comparisons made between independent components within the same type of measurement. This could involve analysis of the same filter or substrate by different methods, such as PIXE versus XRF for iron.

Level 2

Level 2 validation represents comparisons with diverse types of measurements which deliver comparable quantities. For IMPROVE, this refers to totally independent channels such as sulfur x 3 (from PIXE and XRF, Channel A, Teflon) versus sulfate (from IC, Channel B, Nylon).

Level 3

Level 3 validation represents comparisons between totally different groups and techniques operating in a side by side mode. An example of these are the Nitrate and Carbon "Shoot Outs" sponsored by the ARB, 1985 and 1986, and virtually any major field experiment from ACHEX (1972-1973) (Hidy et al., 1974) to the present.

Section 2.02 Example of IMPROVE

The concept of "integral redundancy"

The IMPROVE program, under Tom Cahill, developed the concept of "integral redundancy" as a continuous high Level 2 QA/QC (Malm et al., 1994). In this concept, Level 2 comparisons were an integral part of the monitoring strategy, not just an occasional component or test. Four completely independent channels operated simultaneously, each with its own inlet and flow control, were controlled by a single clock. Each had measurements within it that allowed for Level 1 comparisons and each contributed to Level 2 comparisons for most major components. In all cases, Level 0 QA/QC was done with repeated analyses, blanks, etc.

Channel A	Teflon	Mass (PM _{2.5}) PIXE Na-Fe XRF S-Pb PESA H (organics)	Level 1 Elements (PIXE) vs Elements (XRF) Mass vs reconstructed mass (RCMA)
Channel B	Nylon (denuder)	Ions(IC)	

Channel C	Quartz	OC/EC (TOR)
Channel D	Teflon	Mass(PM ₁₀)

“Integral redundancy” then applied a Level 2 QA/QC via -

Channel A sulfur, (from PIXE) times 3, versus Channel B sulfate.

Channel A organics (from PESA) versus Channel C organics (from TOR).

Channel A RCMA versus Channel C reconstructed mass (TOR).

The operation of these protocols are shown in the annual IMPROVE summary, 1988-1995.

Article III. Impaction - General Concepts

Section 3.01 Theory of Impaction

While any sharp bend of an air stream will result in separation of large particles from the carrier gasses, (e.g., cyclones, virtual impactors, etc.) two configurations allow for calculation of the separation process from basic aerodynamical theory - the single orifice and the infinite slot. These calculations operate without any assumptions as long as limits are respected such as keeping the Reynold's number within reasonable bounds (Marple, 1980, Rabbe et al., 1988). Further, Raabe (1988) has shown that the shapes of the separation curves are all identical and independent of cut point when a dimensionless parameterization is used. This is different from many other configurations such as the MOUDI in which the shape or asymmetry of each stage is different. Finally, impaction theory for these configurations delivers the sharpest particle separation by size that one can theoretically achieve, allow for many closely space stages if desired. The DELTA Group only uses impactors that meet these conditions.

Section 3.02 Validation of Impaction Theory

The theory of Marple (1980) was validated by Rao in his thesis (1979). In addition, Raabe et al. (1988) performed validation tests using several techniques. In summary, there was an excellent match, theory versus experiment, for jetted DRUM impactors. In addition, (Raabe et al., 1988) were able to match the previously published cut points of the Low Pressure Impactor (LPI), also a jetted impactor, but one also using low pressure stages (Herring et al., 197x). Thus, for a variety of conditions, there is abundant evidence that impactor theory and experiment are fully validated for jetted impactors. Slotted impactors share the same theory, but at present lack the validation of the jetted impactor.

Article IV. Impaction in Practice

Since the primary goal of impaction is particle collection, the freedom to use a variety of substrates allows a close match to collection and chemical analysis not available for filters. However, one major limitation of impactors is that they can mis-size particles if they do not stick to the surface upon which they are impacted. In order to avoid mis-sizing by particle bounce, a serious problem in dry, soil aerosols, all impactors need a sticky adhesive coating unless a) the particles are known to be sticky, or b) the particles are so small that bounce is not probable physically. However, one is then limited to no more than a few mono-layers of particles on the impaction substrate, or the sticky coating becomes ineffective (Wesolowski et al., 1978, Cahill 1979). Thus, for 1 μm diameter particles of density 1 g/cm^3 , one achieves a loading of a few hundred micrograms/cm², not much mass for analysis.

Section 4.01 Impaction - DRUM Samplers

(a) Early work - 1969-1979

In 1967, Dale Lundgren mated the well-characterized slotted impactor to a moving impaction substrate on a slowly rotating drum, the 5 stage high flow 110 l/min “Lundgren Impactor” (Lundgren 1967). The advantage of this scheme is that time is retained along the circumference of the drum, and by using a removable substrate, on the impaction medium. Mass was impossible to measure, and chemical analysis by standard methods proved difficult, but the sensitivity of proton induced x-ray emission (PIXE) allowed analysis of samples for a large suite of elements, Na through Pb. An early major use was for studies of California freeways (Feeney et al., 1975). A modification of the Lundgren impactor, the 3 stage Multiday impactor, was used for the large California Air Resources Board aerosol network, a 14 site network that, in 4 years of operation, gathered 14,400 samples in 3 size modes with full compositional analysis, 1973-1977 (Flocchini et al., 1976, Barone et al., 1978, Motellabi et al., 1992) as well as special studies (Ashbaugh et al., 1981; Flocchini et al., 1981, Barone et al., 1984).

(b) Development of Jetted DRUM Sampler - 1985-1987

In response to a growing need for size and compositionally resolved samples for the National Park Service, a new sampler was designed in 1985 (Cahill et al., 1985), modified and calibrated (Raabe et al., 1988). This sampler was based upon a single jet, and since it operated at only 1 L/min, delivered a very small amount of mass suitable only to focused analysis systems such as a PIXE milliprobe. This unit, the Davis Rotating-drum Unit for Monitoring (DRUM) was used extensively 1986 through 1998 for studies in Los Angeles (Cahill et al., 1989), Kuwait (Reid et al., 1995) and the national parks (Cahill and Wakabayashi, 1996, Perry et al., 1997), among other studies. Still, the very small amount of mass limited usefulness to relatively polluted conditions, while the line deposit was difficult to quantify, limiting precision.

Section 4.02 Development of Slotted DRUM Sampler - 1989 - Present

(a) RB Monitoring Sampler MSAM 1988-1990

In response to the need for small, inexpensive aerosol samplers that could monitor major parameters associated with acidic species in remote areas of California, the MSAM (MSAM, 1993) was developed, a combination of filters and a slotted 2 stage rotating drum impactor. The unit was designed, built, tested and field evaluated as part of the ARB Acid Deposition program, but was not widely deployed before the program was terminated. However, the MSAM remains both the smallest IMPROVE-protocol sampler ever built, 25 cm x 15 cm x 8 cm, and the smallest DRUM impactor. Its technical successes led, however, to the IMPROVED DRM (below).

(b) IMPROVED DRUM 1992 - Present

In 1992, a new impactor was designed for visibility studies in the IMPROVE program (Malm et al., 1984). In it, three size classifications were achieved designed to match the needs of Mie Theory for visibility; $2.5 > D_p > 1.15 \mu\text{m}$, $1.15 > D_p > 0.34 \mu\text{m}$, and $0.34 > D_p > 0.1 \mu\text{m}$, plus an integrating afterfilter. The coarsest particles, while optically efficient, are too few in number to have much effect on visibility by the $1/r^3$ dependence on number and mass. The middle group is the heart of light scattering, with very high optical efficiency/particle, expressed as $Q_{\text{scat}} = \sigma_{\text{scat}}/\pi r^2$, the ratio of scattering to the particle area, which can reach values like 5 or 6. In addition, this mode is the peak of the Accumulation Mode (Whitby et al., 1975) and has high mass and many particles. The finest stage normally possesses many particles, but since the $0.34 \mu\text{m}$ cut point is set where $Q_{\text{scat}} = 1.0$ and dropping rapidly, the particles are highly inefficient in scattering light. This sampler, because it lays down a 6 mm wide strip instead of a line, is much easier to analyze and has far better precision than the jetted drum configurations (Cahill et al., 1995). Finally, the increased flow of 10 L/min gives 10 times more mass to analyze than the 1.0 L/min jetted DRUM. A recent example is shown in (Perry et al. 1999) in which the increased mass allowed operation even in the very clean conditions at the NOAA Mauna Loa Observatory, 3.4 km high.

(c) DELTA 8 DRUM 1999 - Present

In 1999, the DELTA Group began a process to convert an existing jetted 8 drum impactor to the slotted configuration of the very successful IMPROVED 3 DRUM. Professor Otto Raabe ran his aerodynamical model for 6 mm slots, generating cut points that better met the needs of Mie Theory than the jetted DRUM, with the increased flow to 10.8 L/min and the better precision of the IMPROVED DRUM (Raabe, private communication).

Table 1 Parameters of the DELTA DRUM Slotted Drum Impactor

The width of the mass at full width, half maximum, W_{mass} , represents the measured footprint of a non-rotating DRUM, accurate to about $\pm 15\%$. This results in a resolution in time using a 42 day rotation period (4 mm/day) given in T (hr). The after filter was not used in this work.

Stage No.	W (s) cm	L Cm	S cm	P out kPa	Re	u out m/s	ECD ae, μm	W (d) μm	ΔTime hr
1	0.360	0.6	1.44	101.3	2231	7.7	5.0	750	4.5
2	0.163	0.6	0.65	101.1	2810	17.1	2.5	500	3.0
3	0.073	0.6	0.29	100.2	3195	38.3	1.15	300	1.8
4	0.049	0.6	0.20	98.3	3331	58.3	0.75	265	1.6
5	0.038	0.6	0.15	94.9	3416	77.4	0.56	240	1.4
6	0.026	0.6	0.11	86.8	3575	122.2	0.34	245	1.8
7	0.024	0.6	0.10	75.1	3692	156.0	0.26	180	0.9
8	0.021	0.6	0.10	39.7	4595	315.9	0.09	175	0.9
filter									

This impactor (along with an IMPROVED DRUM) was deployed in the BRAVO study in Big Bend NP, July - October 1999, and operated with essential no loss of samples. The time resolution was obtained by the size of the analytical beams used, and could be low as 1 hr when analyzed at the synchrotron x-ray fluorescence microprobe of the Advanced Light Source, Lawrence Berkley NL.

The important point to remember is that the requirement for field labor for a DRUM sampler is far, far less than for filter samplers, and in many case there is no field labor at all once the sampler is plugged in. In standard operation, the DRUM (3 or 8) will collect 504 samples in 42 days at 2 hr resolution, each sample with 3 to 8 size modes. Note that just buying the filter media for 504 samples on Teflon is \$2,500 for filter samplers.

In 2000, in response to the ARB sponsored studies at the Fresno Supersite, the DELTA modified to directly match the 16.7 liter/min flow of standard PM10 heads. This was done by simply extending the length of the slot without changing any other parameters, an option only available to a slotted DRUM. This has the additional advantages that the wider slot allows dual aluminum-Mylar substrates. While this is not recommended for coarse stages in dry conditions due to particle bounce on the aluminum, it works well for most conditions while delivering an aluminum strip ideal for laser desorption ionization time-of-flight mass spectrometry and thus speciated organic matter.

(d) DELTA 3-DRUM 2000 - Present

For the NSF-funded ACE-Asia program, 10 new 3 DRUM samplers were purchased from Integrity Manufacturing (RTP, NC) with revised parameters. The flow was raised to 23 l/min by lengthening the slots while keeping all other parameters fixed. The flow was designed to match the IMPROVE cyclone, which was then added as a pre-cut to the sampler.

(e) DELTA 5-DRUM 2008 with Streaker Afterfilter

At the suggestion of Dr. Willilam Wilson of the US EPA, a version of the Drum Sampler was prepared with cut sizes of 10, 2.5, 1.0, 0.25, and 0.1 μm to provide information most suitable for use in epidemiological analyses and source category apportionment. A modification of the Florida State University "streaker" sampler was used to replace the after-filter in order to provide the same time resolution for the after-filter as for the

impaction stages. This version of the Drum Sampler operates at a flow rate of 16.7 l/min (the flow rate of the US EPA FRM for PM10) and uses the same inlet as the FRM.

Section 4.03 Airflow Volume

Airflow volumes are set by the critical orifice at Stage 8. Thus, the flow is fixed as long as no change in pressure occurs in the 7 stages in front of the orifice. The flow is validated via a non-critical orifice placed over the inlet, and calibrated quarterly to an absolute standard, a Collins spirometer.

Section 4.04 Particle Cut Points

(a) Jetted DRUMs

The particle cut points for the jetted DRUM are fully established by theory and extensively validated in both the jetted DRUM sampler and the Herring Low Pressure Impactor (Raabe et al., 1988).

(b) Slotted DRUMs

The particle cut points for the slotted DRUM are fully established by theory but still lack validation in both the jetted DRUM sampler and the Herring Low Pressure Impactor (Raabe et al., 1988).

Section 4.05 Sample Collection

(a) University of Minnesota studies

The Ph. D. Thesis of Rao (1979) presented a detailed analysis of particle collection behaviors, and was the source of present MOUDI recommendations that all surfaces be coated with anti-bounce coatings. With such coatings, Rao showed excellent prevention of particle bounce.

(b) UC Davis Studies

For the slotted DRUM impactor, the first comparison of two slotted DRUM impactors (other than the historical data in the period 1973-1979) was the MSAM final report (MSAM 1993) for tests done in Sacramento. The key finding was that the precision of the slotted DRUM was much better than the jetted DRUM, $\pm 5\%$, versus $\pm 15\%$ for a typical jetted DRUM, for both iron (a soil tracer) and sulfur.

Section 4.06 Resolution in Time

(a) Theoretical

The resolution in time is set by the rate of rotation and the drums in the DRUM sampler, the width of the slot, and the size of the analytical beam. With complete control of the analytical beam for S-XRF, STIM, and LDI TOF/MS, the latter does not factor into the equation as long as it is less than 100 μm or less in size.

The time resolution could be better than that set by the slot width of each impaction stage, as only within the slot are velocities high. There are good physical reasons why the resolution could be better than the slot width, as particles will tend to center in the slot due to drag at the walls. Thus, the values below must represent the poorest possible time resolution.

Table 2 Effect of Slit Width and Rotation Rate on Time Resolution (Theoretical).

DRUM stage	Size cuts (μ m) from theory	Slot widths (μ m) from theory	2 week rotation rate (12 mm/day)	4 week rotation rate (6 mm/day)	6 week rotation rate (4mm/day)
1	10 to 5.0	3600	7.2 hrs	14.4 hrs	21.6 hrs
2	5.0 to 2.5	1630	3.3 hrs	6.6 hrs	9.8 hrs
3	2.5 to 1.15	730	1.5 hrs	3.0 hrs	4.4 hrs
4	1.15 to 0.75	490	1.0 hrs	2.0 hrs	2.9 hrs
5	0.75 to 0.56	384	42 min	1.5 hrs	2.3 hrs
6	0.56 to 0.34	265	32 min	1.1 hrs	1.6 hrs
7	0.34 to 0.24	240	29 min	1.0 hrs	1.4 hrs
8	0.24 to 0.09	215	26 min	1.0 hrs	1.3 hrs

(b) Empirical

Scans have been made over actual slotted DRUM impactor samples using the S-XRF system from line samples at Mauna Loa Observatory (xxx) and by mass by STIM on test samples provided to LLNL (Graham et al., 2001)

The measured widths of the deposit, full width half maximum, can then be compared to the slot width, as shown below. It is interesting to note that for the larger stages, the measured width of the deposit is much less than the width of the slot.

Table 3 Measured Full Width at One-Half Maximum of the Aerosol “footprint”.

DRUM stage	Size cuts (μ m) from theory	Slot widths (μ m) From theory	Deposit width via S-XRF (μ m) (FWHM)	Deposit width via STIM (μ m) (FWHM)
1	10 to 5.0	3600	750 \pm 100	
2	5.0 to 2.5	1630	500 \pm 75	
3	2.5 to 1.15	730	300 \pm 50	
4	1.15 to 0.75	490	265 \pm 40	
5	0.75 to 0.56	384	240 \pm 30	
6	0.56 to 0.34	265	245 \pm 25	
7	0.34 to 0.24	240	180 \pm 25	
8	0.24 to 0.09	215	175 \pm 25	

In the DRUM impactor, typical rotation rates are 2 week, 4 week, and 6 week, covering in all cases 168 mm. Using the measured deposit widths from S-XRF, we can convert slit

widths to time integration, stage by stage, to establish validated time resolution as a function of DRUM particle size and rotation rate.

Table 4 Effect of Slit Width and Rotation Rate on Time Resolution (measured).

When compared to the theoretical widths in Table 6, the deposit is significantly narrower than the slit, especially for the coarser particles, leading to much better time resolution than anticipated theoretically.

DRUM stage	Deposit width via S-XRF (μm) (FWHM)	2 week rotation rate (12 mm/day)	4 week rotation rate (6 mm/day)	6 week rotation rate (4mm/day)
1	750 ± 100	1.5 hrs	3.0 hrs	4.5 hrs
2	500 ± 75	1.0 hrs	2.0 hrs	3.0 hrs
3	300 ± 50	36 min	1.2 hrs	1.8 hrs
4	265 ± 40	32 min	1.1 hrs	1.6 hrs
5	240 ± 30	29 min	1.0 hrs	1.4 hrs
6	245 ± 25	29 min	1.0 hrs	1.5 hrs
7	180 ± 25	18 min	36 min	54 min
8	175 ± 25	18 min	36 min	54 min

It should be noted that Stage 1 plus 2 are the “coarse mass” fraction between 2.5 and 10 μm diameter, and are often dominated by soils. Most metals occur in the sub-micron stages, 4 through 8, which have better time resolution.

While impaction theory assumes a “semi-infinite slot”, in practice this is impossible. The first few stages of the DRUM impactors have slot lengths only slightly longer than slot widths, leading to the possibility of mass escaping laterally from the impaction area and thus modifying the conversion constant, which uses slot length time rotation rate to get the area of the deposit. In practice, some mass is seen laterally, but the amount was not known. If the mass seen was merely the result of a soft lateral cut point, and the mass came exclusively from locations quite close to the slot ends, then negligible error would be incurred by using the center of the deposit for the point of analysis.

Table 5 Measured Versus Theoretical Lengths of the Deposit Along the Slot length.

Both long slot samplers show excellent agreement with the theoretical values, while the standard 8 DRUM is systematically longer by about 8%.

Sampler	Cut points μm	Physical length Mm (to ± 0.5 mm)	Deposit length mm
Fresno 8 DRUM	10 > Dp > 5.0	10.0	10.4 \pm 0.1
#1			
#3	2.5 > Dp > 1.15	10.0	10.1 \pm 0.1
#4	1.15 > Dp > 0.75	10.0	10.0 \pm 0.1
ACE-Asia 8 DRUM	\approx 12 > Dp > 5.0	6.05	6.4 \pm 0.1
Uji - #1			
#2	5.0 > Dp > 2.5	6.05	6.8 \pm 0.1
#3	2.5 > Dp > 1.15	6.05	6.7 \pm 0.1
#4	1.15 > Dp > 0.75	6.05	6.4 \pm 0.1
ACE-Asia 8 DRUM	\approx 12 > Dp > 5.0	6.05	5.3 \pm 1.0
Tango - #1			
#2	5.0 > Dp > 2.5	6.05	6.45 \pm 0.1
#3	2.5 > Dp > 1.15	6.05	6.4 \pm 0.1
#4	1.15 > Dp > 0.75	6.05	6.4 \pm 0.1
#5	0.75 > Dp > 0.56	6.05	6.45 \pm 0.1
ACE-Asia 3 DRUM	2.5 > Dp > 1.15	10.0	10.0 \pm 0.1
#A			
#B	1.15 > Dp > 0.34	10.0	9.9 \pm 0.1
#C	0.34 > Dp > 0.1	10.0	10.4 \pm 0.1

The deposits from three types of slotted DRUM samplers were scanned along the slot length in the soft beta/optics system of the DELTA Group. The values were then integrated to get the effective slot length. Contrary to our expectations, only a very slight enhancement was seen in the effective slot length for the larger stages. The values for stage #1, Tango, have been discounted because one edge of the deposit was very close to the mounting frame, and it is not certain that all the deposit was seen. The material seen beyond the end of the slot came exclusively from locations close to the end of the slot. This means that measurements made in the center $\frac{1}{2}$ of the deposit are correct assuming the proper effective slot length is used, with the possible exception of Stage #1. The wide slot 8 DRUM (Fresno) and the Integrity wide slot 3-DRUMs are 1.5% \pm 1% and 1.0% \pm 1% greater than the physical slot length. The results for the ACE-Asia 8 DRUMs, however, showed a systematic deposit length 7.4% \pm 2.4% longer than the physical slot length. This has been taken into account in the revised conversion factors that reduce ng/cm² to ng/m³.

(c) Establishment of the Uncertainty in Time

In order to establish the sensitivity of 24 hr averaged filter data to uncertainties in time in the DRUM data, the existing data at Fresno on the DELTA 8 stage slotted DRUM was deliberately shifted in time by either + 6 hrs forward or - 6 hrs backward. Thus, if the original data were 0000 to 0000, + 6 hrs gave 0600 to 0600, and - 6 hrs gave 1800 to

1800. The results are shown below for each size range for a typical transition metals zinc (mostly anthropogenic, primary pollutant), iron (mostly natural, primary pollutant), and sulfur (mostly anthropogenic, secondary pollutant).

Table 6 Sensitivity Tests for Uncertainties in Time.

DRUM Stage #	Zinc		Sulfur		Iron	
	+ 6 hrs	- 6 hrs	+ 6 hrs	- 6 hrs	+ 6 hrs	- 6 hrs
1	0.08	0.10	0.08	0.10	0.08	0.08
2	0.10	0.10	0.13	0.17	0.09	0.11
3	0.15	0.15	0.19	0.16	0.12	0.18
4	0.20	0.14	0.16	0.10	0.11	0.15
5	0.17	0.12	0.13	0.12	0.11	0.10
6	0.36	0.28	0.18	0.41	0.13	0.20
7	0.30	0.20	0.25	0.12	0.26	0.27
8	0.27	0.29	0.28	0.13	0.27	0.47
Average	0.18		0.20		0.16	(- 2 pts)

In summary, a 6 hr shift in either direction gives a mean uncertainty of 18%, or 3%/hr. The uncertainties are larger in the finer size modes where extreme variations in pollutants occur and slot widths are narrow, less in the coarser modes with their larger slot widths.

The uncertainty in time for DRUM sampling is critically dependent upon the availability of time data during the DRUM sampling. The DQAP protocols require on site personnel to record start and stop times and put time markers on the DRUM weekly. The uncertainty in time is critically dependent on this protocol, and lack of any one of the actions will impact the uncertainty in time on the data. For a 42 day rotation rate, sub-micron stages –

Protocol (assumes no power outages > 15 min)	Maximum uncertainty
Start time only	7.5 ± 3.0 hr
Start and stop times	3.7 ± 1.5 hr
Start and stop times, one time marker	1.5 ± 0.75 hr
Start and stop times, 2 or more time markers	1.2 ± 0.30 hr

The maximum uncertainty, 7.5 ± 3.0 hr (0.7%) was established in 42 days in the 1999 EPA BRAVO study, has been reduced to less than 1.5 hr (0.15%) at those sites where intermediate time markers were used with protocols developed in the large NSF ACE-Asia study, during which we took over 80,000 DRUM samples.

Section 4.07 Summary of Level 0 Validations

The conversion from the values in ng/cm² generated by beam based analytical techniques to ng/m³ concentrations in ambient air requires a conversion constant CC cm²/m³.

Conversion constant = Area of the deposit in cm² / volume of air in m³.

The area of deposit is given by the rotation rate times the effective slot length (above) while the volume of air is given by the flow rate times the integrating time. Of these parameters, the time of sampling and rotation rate are known to < 0.1%, the airflow set by the critical orifice has an error less than 1%, and the effective deposit length to better than 2%. In summary, then, the propagated error from the conversion constant is on the order of 2%.

DELTA Group 8-DRUM Sampler Operating Instructions and Description, PM10 Modification

October 2001

The standard DELTA Group DRUM sampler a modified 8-DRUM sampler derived from a rotating substrate Lundgren type cascading inertial impactor. Modifications include an Andersen PM10 inlet, which operates at 16.7 ($\pm 5\%$) liters per minute as well as specially designed slotted orifice to accommodate this airflow. The orifice impact a 1 cm wide deposit on the substrate and maintain airflow at 16.1 ($\pm 5\%$) liters per minute when the sampler is properly maintained. Air is introduced through the inlet and is sequentially impacted onto the rotating substrates (drums) according to aerodynamic diameter. The substrates are a lightly grease (Apiezon-L in toluene) coated eighth mil (0.000125 inches thick) Mylar specially prepared in the DELTA Group Laboratory at the University of California, Davis. The substrate is clean and contaminant free and must remain so for high sensitivity analysis (i.e. DO NOT TOUCH THE SUBSTRATE). In addition to these detailed DRUM operating instructions (SOP), there is an animated PowerPoint presentation detailing drum function and cleaning with pictures, and a checklist on each sample logsheet for quick reference. In the even that any of these instructions are insufficient or unclear please use the contact information in section H at the end of this document.

Definitions

1. 8-DRUM: the 8-stage Davis Rotating Unit for Monitoring sampler described above.
2. audit (flow audit): the practice of measuring the flow of air through the inlet of the DRUM sampler.
3. audit device (external): an instrument for measuring the sampler airflow independent of the sampler itself. For the DRUM this consists of a calibrated Magnehelic attached to a specially designed flow calibrated inlet adapter.
4. drum: the anodized aluminum cylinder that supports the substrate.
5. DRUM cup: the cavity on the sampler between orifice where the spindle and drum are located.
6. drum holder: a capped plastic container with a red insert containing a spindle. Used for protection or exposed and un-exposed drums during storage and transport.
7. critical orifice: the final orifice of the sampler which sets the flow rate through the inlet. It is physically located between stages 7 and 8.

8. orifice: the anodized aluminum cylinder separating sampler stages with a rectangular slotted hole through which ambient air passes.
9. spindle: The keyed shaft in the DRUM which supports the drum during sampling and rotation.
10. substrate: the coated Mylar material on to which aerosol sample is impacted.

Overview

1. Operation of the DRUM sampler consists of installation of the inlet, installation of drums with substrate, motor rotation and gear engagement, pump hose connection, and pump operation. Rotation rate and flow are pre-set and cannot be adjusted by the operator.
2. While actual start and stop times are not critical, knowledge of the exact time (+/- 15 minutes) is. The operator MUST record start and stop times for beginning, end, interim time markers (see #B5 below), and planned or unplanned events (e.g. power outages) when known. Preferred starting and/or stopping time is 12:00 noon. Since these times are not always practical (e.g. when changing drums between sampling which requires 30-60 minutes of work) adherence when possible is ideal. A start time for each strip of approximately noon is preferred when it does not prevent several hours of sampling (e.g. when drums must be changed in the early morning to avoid the sun).
3. The EPA protocol for the PM10 inlet requires cleaning approximately each 500 hours of operation. Since the DRUM operates continuously, this corresponds to 3 weeks of sampling. Currently, two inlets are provided with the DRUM allowing rapid change-out of inlets and sufficient time for inlet preparation between change-outs.
4. The rotation of the substrate is set for 6 weeks of sampling (i.e. 6 weeks for 7/8 rotation of the drum circumference). There is sufficient substrate to allow sampling on clean/coated Mylar within this rotation period. The operator should ensure that sampling on the 1/8 circumference where tape is not present does not occur. In the event that the 6-week sampling period is not followed (i.e. shorter sampling period due to holiday or scheduling conflicts) the following sampling period must be adjusted accordingly. Essentially this means that less than 6 weeks of total sampling is allowed under this protocol, but more than 42 days is not.
5. The DRUM is protected from over-sampling on the substrate by use of a micro-switch keyed to the drum rotation. If the 42 day sampling period is exceeded the pump will continue to operate without further substrate rotation. In this case the end time will not be precisely known, but the prior 42+ days sample will not be lost.
6. In order to more precisely determine sampling time related to ambient sample, a “negative” time marker is required approximately halfway in each 6 week sampling period. The “negative” time marker consists of turning off the pump for a predetermined period of time (usually 12 hours corresponding to 2 mm of clean substrate) while allowing the drum to continue rotation. The clean portion on the substrate will be visually evident when mounting the substrate for analysis.

7. Flow is maintained by means of a critical orifice which doubles as the orifice for the final impactor stage (#8). Adjustment of flow is not possible with this sampler. However, flow audits must be performed to ensure proper flow and hence calibrated particle cut-points while sampling. Reduced flow (below 16.1 l/min) may indicate clogging of the orifice. Increased flow may indicate a leak in the sampler. External audits should be performed at each inlet change-out at a minimum (i.e. every three weeks). More frequent flow audits may be required due to increased aerosol concentration, especially during an “event” or wintertime inversion periods. Since the sampler has no internal flow audit device, the external audit will serve all auditing purposes.
8. Rotation of the drum in Stage #1 is evidenced by the movement of the indicator mark on the drum through the clear drum housing cover. Movement is slow, 4 mm/day, and will not be visually obvious for time periods less than 6 hours. The operator must periodically check the drum rotation to confirm adequate movement in a given time period. This movement need only be estimated, however, as there is no adjustment capability (i.e. working or not working). Extended power outages will be evident when mounting for analysis and should be accounted for if known (see #B2 above).

Substrate/drum Removal and Installation

1. DRUM sampler consists of 8 drums coated with Mylar substrate. Since sequential particle sizing and capture is accomplished by the impaction of PM on to the substrate, it is critical to know the order of the drums (i.e. 1 through 8 must be marked).
2. Drums will arrive onsite pre-loaded with substrate and sequentially numbered from the DELTA lab at UCD. In the event that the drums are not numbered, numbering should be accomplished prior to installation. Use of indelible marker such as a “Sharpie” or “White-Out “ pen is typical.
3. Each drum will come in a plastic drum holder which protects the drum when it is not installed in the sampler. Exposed drums are placed in clean drum holders and capped individually (i.e. store each drum before moving onto the next). If the drum holder is obviously dirty, it must be cleaned with KimWipe and ethanol prior to use.
4. When removing the drum from the sampler, the operator must take care not to touch anything to the Mylar substrate. The center part of the drum has a cylindrical handle for use when handling the drums. Care in drum removal, especially when removing from the spindle, is imperative.
5. Sequentially remove and store each drum, making certain that the drum is properly marked with sampler stage.
6. Clean the sampler as outlined in section F (below).
7. Insert un-coated drum into stage 3. Fully depress drum onto keyed spindle to ensure proper alignment. Leave cover open to verify alignment.
8. Reset rotation using provided key on stage 2 by carefully turning COUNTER-CLOCKWISE until drum in stage 3 is properly aligned. Proper alignment is indicated when the mark on the drum is in the start position, just left (or counter-clockwise) of 12 o'clock (approximately 11:50 o'clock).

9. Sequentially insert properly marked drums in sampler.
10. Verify proper alignment on all stages. Since the sample is impacted on the Mylar substrate, it is important that the tape affixing the substrate to the drum not interfere with sampling. This is accomplished by keeping the start mark slightly left (or counter-clockwise) of the orifice/sampling vertical line. Essentially, we attempt to maximize sampling time by maximizing substrate exposed while preserving sample analysis capability by only sampling on appropriate substrate (i.e. the Mylar).
11. Note that alignment for stages 1-4 is with the mark on the drum vertical at the top of the sampler and opposite for stages 5-8 (i.e. vertically down for left side of sampler).
12. Cover each cup with clean cover to prevent accidental damage to drums from falling out of sampler. Reserve the clear plastic cover for stage 1 for future rotation verification.
13. When inserting drums make certain that drums are fully depressed onto keyed spindle. If they are not properly seated the covers will not fit properly and proper rotation will not occur.
14. Cleaned sampler is ready for operation when all un-exposed drums are properly aligned, loaded, seated, and covered.

External Audit of DRUM Sampler

Although there is no flow adjustment capability for the DRUM sampler, external audits are necessary. An external audit serves to ensure proper primary aerosol sizing through the PM10 inlet as well as aids in identifying potential problems with the sampler (e.g. orifice clogging). Auditing of the DRUM is accomplished by use of a calibrated Magnehelic and inlet adapter. It is important that the combination of Magnehelic/adapter remain constant after calibration (i.e. re-calibration must be performed if a new adapter is used). The Magnehelic is a differential pressure gauge that measures a pressure change between a high and low pressure point in the sampler system. Using the same adapter ensures that the pressure change for a given flow rate is a constant. Calibration will be performed in the DELTA Group laboratories at UCD. Annual re-calibration will be performed by the DELTA Group. Re-calibration is also necessary if any of the following occur: Sudden blow or jolt to Magnehelic such as from a drop, exposure to extreme temperature such as being left for extended periods in direct sunlight, extreme pressure differentials such as high altitude flight (where both high and low ports are NOT exposed to the same pressure) or exposure to a vacuum pump. The operator MUST contact the DELTA Group if re-calibration is warranted.

1. Flow audit is best accomplished in calm (i.e. little or no wind) weather conditions.
2. Remove PM10 inlet head from sampler. Leave stack (tubing) in place.
3. Insert calibrated adapter into inlet side of remaining stack.
4. With Magnehelic in upright/vertical position note and record pressure differential value.
5. If it is necessary to perform audit when windy conditions are present, estimate “average” reading. Verify reading at a later time when calm conditions are present if practical.

6. Remove calibrated adapter when audit is complete.
7. Replace PM10 inlet head.
8. NOTE: It may be necessary to use a small amount of silicone grease (provided) to insert adapter and/or inlet head. Use sparingly as necessary.

Maintenance and Operation Schedule

1. Substrate/drum replacement: Every 6 weeks maximum.
2. PM10 inlet head: Every 3 weeks.
3. External flow audit: Each week.
4. Rotation confirmation: Twice weekly and 1 day following change-out.
5. Time stamp “negative” mark: Every 3 weeks.
6. DRUM sampler cleaning: Every 6 weeks unless flow audit indicates more often.

DRUM Sampler Cleaning

Periodic cleaning of the sampler is required and generally varies depending on the sampling environment. At Fresno, a full sampler cleaning each 6 weeks during drum change-out is typically sufficient. More frequent cleaning may be indicated by reduced flow as measured by the audit device.

1. With sampler properly downloaded and DRUM cups empty of drums, begin cleaning procedure by wiping cups with KimWipes and ethanol to remove obvious dirt.
2. Using ethanol wetted narrow strip of paper (provided, less than 1 cm width) gently floss stage 8 orifice. To floss, insert paper into orifice and wet with ethanol from wash bottle. Ethanol will wick into orifice.
3. Move paper back and forth and repeat until paper is removed clean. Several strips may be required or clean part of paper may be used as necessary.
4. Repeat flossing on stages 7 through 1 working sequentially in reverse.
5. Flossing stage 5 (at bottom of DRUM) does not allow handling of both ends of paper. Carefully clean to make certain that paper is not jammed into orifice causing blockage. Make certain that no debris remains in bottom cavity of sampler between stages 4 and 5.
6. Back-blow orifice using provided dry “air” electronics cleaner (i.e. blow from narrow to wide end to ensure blockage removal).
7. Periodically blow out DRUM cup with dry “air” to remove large debris that may cause orifice blockage.
8. Perform final cup wiping using KimWipes and ethanol.
9. Perform final cup dusting with dry “air.”
10. Clean cup covers (especially o-ring and sample exposed face) with KimWipes and ethanol.

Summary Operating Procedure

Each 6 weeks as indicated on schedule:

1. Record ending vacuum reading from gauge on back of DRUM sampler.
2. Audit ending flow of DRUM prior to substrate removal and record (Section D).
3. Turn off rotation and pump, record time/date.

4. Sequentially remove and properly store exposed drum substrates. Note correct markings indicating sampler stage. Record any appropriate notes on logsheet (Section C).
5. Clean DRUM using dry “air,” KimWipes, and ethanol provided as described in Section F.
6. Reset rotation to start by rotating spindle COUNTER-CLOCKWISE with provided key on stage 2 or 3. Verify start with uncoated drum in stage 1. Start position indicated by drum mark just left (or counter-clockwise) of 12 o’clock position (i.e. 11:50 o’clock position). This ensures sample impaction on Mylar and not tape on the coated drums.
7. Sequentially install unexposed drum/substrate as described. Note proper stage marking. Verify correct installation with starting mark on drum and proper key position on spindle. Make certain to fully insert drums to ensure proper rotation. Cover each drum cup after proper installation to prevent the drum from falling out while loading additional stages. Take care to properly install cover to ensure vacuum seal and not damage the o-ring. Reserve the clear plastic cover for stage 1 for future rotation verification.
8. Power on pump and DRUM motor. Record time and date. Verify DRUM power by orange light on rear of DRUM. Pump operation is audibly verified. Power on should occur at 12 noon on start date.
9. Record starting vacuum reading.
10. Audit starting flow and record.
11. Install clean PM10 inlet head.
12. Verify rotation as indicated on schedule (after 1-3 days) and note on logsheet.

Each 3 weeks as indicated on schedule:

13. Record vacuum gauge reading.
14. Audit flow as described and record.
15. Perform 12 hour “negative” time marker by turning off pump at midnight, but leaving sampler rotation on. Record time and date of pump off. Pump should be manually restarted at 12 noon and verified.
16. Replace PM10 inlet head with cleaned head.
17. Restart pump, record time/date.
18. Audit flow and record.
19. Record vacuum gauge reading.

Sampler Support

Support for the DRUM sampler is provided by the DELTA Group at the University of California, Davis. Approximately every 6 weeks the DELTA Group will FedEx new substrates to the user along with any other requested materials (e.g. dry air, KimWipes, ethanol, etc.). The exposed substrates will be returned to DELTA with log information regarding maintenance, flow audits, start and stop times, interim non-sampling times, and unusual event information (e.g. strange weather, noticeable PM source like fires nearby, etc.). Please contact the DELTA Group lab with problems or questions.

Normally, each experiment will have a designated contact, usually Steve Cliff or Michael Jimenez-Cruz or Tom Cahill

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DELTA Group Quick Reference: Downloading Strips

1. Gather all site information and logsheets
 - a. Site name and operator
 - b. Sampler ID and Rotation rate
 - c. Start Date and Time
 - d. Stop Date and Time
 - e. Any time markers during sampling
2. Make a chart for each stage in strip downloading book that would have measured length, mounted length, and theoretical length. Note: ALL MARKINGS ON DRUMS MUST BE MADE WITH PERMANENT INK
 - a. Decide on site code. Sampling site name should clearly identify the site, sampler and project while minimizing length. As well it must be unique. DO NOT over-truncate the site name such that there is confusion between sites (e.g. TA vs. TN representing Taiwan vs. Tango). Full sample code truncation will occur at ALS during analysis.
 - b. Calculate the theoretical length based on rotation rate and known start and stop (if applicable).
 - c. Measure the length of deposit on the drum using cylindrical drum scale.
 - d. Record the beginning, interim markers and end of deposit.
 - e. Rectify differences between theoretical and actual sample data.
 - f. Get enough strip frames for downloading, and mark all with sample information. Mark opposite (blue) side with start point (on right at top) to avoid confusion in downloading and analysis.

- g. Minimum information on strip frames: site name, project name, dates operated, rotation, stage, size cut, and questionable sampling information.
- h. Mark the start, interim markers and end positions on the strip near edge away from any deposit.
- i. Measure the length of the deposit on strip frame.
- j. Mark start, interim markers and end positions from sample measurement on strip frame.
- k. Download strips from drum to strip frame, starting the deposit at a position higher than 3.
- l. Make certain substrate is flat, stretched appropriately, and secured. Tape should not extend beyond frame as it will interfere during analysis.
- m. Record any pertinent information in book (e.g. sample compromised due to touching, scraping, falling, etc.).
- n. Properly store samples in protective case for transport and archive.

Appendix A - Raabe et al., Calibration Studies of the DRUM Impactor

Raabe, Otto G., David A. Braaten, Richard L. Axelbaum, Stephen V. Teague, and Thomas A. Cahill. Calibration Studies of the DRUM Impactor. *Journal of Aerosol Science*. 19.2:183-195 (1988).

Appendix B

SOPs for S-XRF Analyses

Beginning in the 1990s, the DELTA Group was formed to advance the analytical capabilities needed to match the advances in impactor design. Before 1997, virtually the only method of analysis widely used was proton induced x-ray emission (PIXE) typically with mm beam resolution. However, cost was high, roughly \$10./min at UC Davis (with quality assurance and set-up), or roughly \$840./strip at 2 mm increments. Thus, a full 8 drum slotted DRUM sampler would cost \$8,400./DRUM, 6 hr time resolution, at a sensitivity of roughly 30 ng/m³.

The philosophy was to develop and adapt methods that were non-destructive, so that repeated measurements could be made, from the simplest and cheapest to the most complex and expensive, depending on the need of the user.

Since 1997, the following techniques have been developed. Certification of accuracy and precision is ongoing, with two major projects involving the Fresno and Baltimore EPA Supersites, and smaller studies at the Houston Supersite and at Cheju Island, Korea, during ACE-Asia. In order of development, they are:

Section 4.08 Synchrotron-Induced X-ray Fluorescence (S-XRF)

This is basically a form x-ray fluorescence with the polarized x-ray beams. Note that we had on occasion used S-XRF on filters and impactors for the Kuwait oil fire studies (Cahill et al., 1992) and other special uses, but the difficulty and access was such as to discourage regular use. The S-XRF microprobe at the Advanced Light Source, Lawrence Berkeley NL provided us support and encouragement to make this procedure widely applicable for aerosol studies. The DELTA Group spent 4 years developing a white beam, 4 keV to 18 keV, with a beam spot size matched to the DRUM impactor impaction “footprint”. Typically, we obtain about 0.1 ng/m³ sensitivity in a 30 sec analysis run at a sampling time bite of typically 3 hrs. for elements sodium through lead. Figure 1 shows an example of the spectrum of the 1.15 > Dp > 0.34 μm mode from a 3 stage DRUM sampler run near the Houston EPA Supersite, August, 2000. The sensitivity data are shown in Table 2 as of July, 2001, as configured for the NSF ACE-Asia program.

Figure 1 Example of an S-XRF Spectrum.

This spectrum was taken during ACE-Asia from a DRUM sampler. The substrate was Apiezon-L coated Mylar, and the first 2 peaks on the left are the carbon and oxygen in Mylar (C₁₀H₈O₄). Note the absence of significant nitrogen. The next 4 peaks are sodium, magnesium (both small), aluminum, and silicon, followed by phosphorus and the largest peak, sulfur (typical of fine aerosols in China because of the coal burning). There is essentially no chlorine, and the small peak in the valley is argon in the residual air (the vacuum was about 1 torr). After Ti V, Cr, and Mn, the next largest peak is iron, followed by Ni, Cu, Zn, bromine and lead. As important are the peaks seen, the absence of peaks is also very useful information. Mercury, for example, is not seen in this spectrum, but was seen commonly in Beijing, PR China.

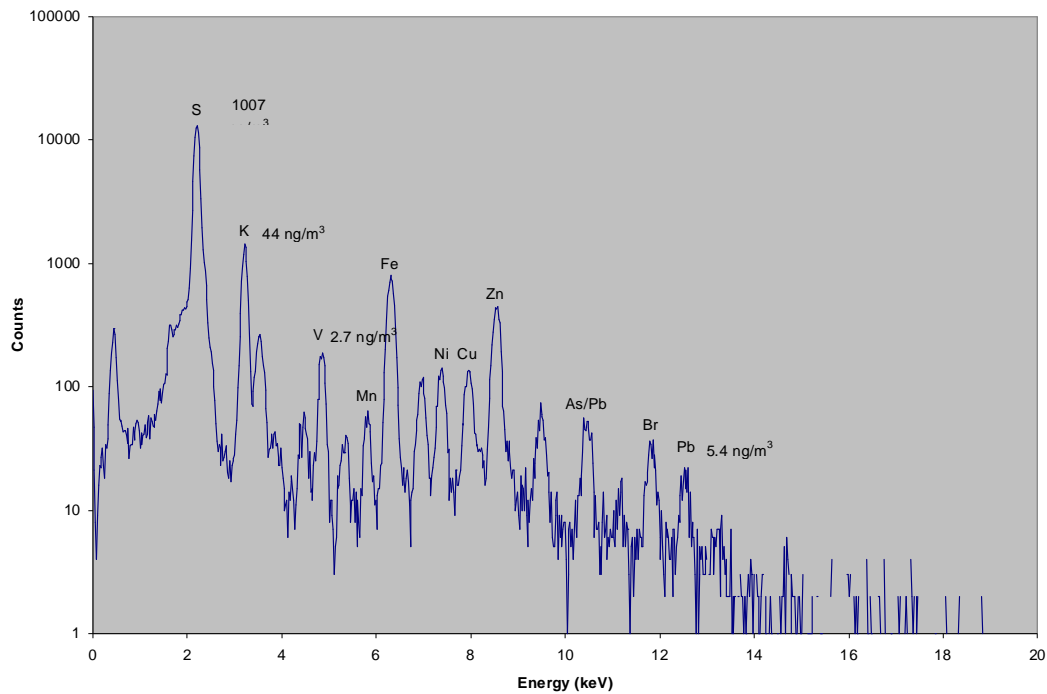


Table 7 Comparison of Sensitivities

Comparison of sensitivities				
RTI prices/summer, 2000				
IMPROVE Malm et al, JGR 1994				
DELTA July, 2001				
on Teflon filters				
RTI	RTI	RTI	IMPROVE	DELTA
XRF	RTI XRF	RTI XRF	PIXE/XRF	S-XRF
\$70	(8/2000)	(8/2000)	(> 1992)	(8/2001)
	\$70./	\$70./	\$72./	\$25/
	filter	filter	filter	filter
Element		A = 8 cm2	2 cm2	2 cm2
		(WINS)	(IMPROVE)	(DELTA)
	ng/	ng/	ng/	ng/
	filter	cm2	cm2	cm2
Na#	1.206	150.0	100.00	13.8
Mg#	0.145	18.0	53.90	8.2
Al	0.064	8.0	30.80	5.5
Si	0.045	5.6	23.10	2.6
P	0.039	4.8	20.00	2.9
S	0.032	4.0	20.02	3.1
Cl	0.039	4.8	21.56	0.8
K	0.024	3.0	12.32	0.6
Ca	0.016	2.0	9.24	0.3
Ti	0.011	1.4	6.16	0.1
V	0.008	1.0	6.16	0.1
Cr	0.008	1.0	4.62	0.1
Mn	0.013	1.6	4.62	0.1
Fe	0.010	1.3	1.85	0.4
Co	0.007	0.9	0.92	0.2
Ni	0.007	0.9	0.92	0.2
Cu	0.007	0.9	0.77	0.1
Zn	0.008	1.0	0.77	0.1
Ga	0.017	2.1		0.1
Ge	0.016	2.0		0.1
As	0.014	1.7	0.46	0.1
Se	0.011	1.4	0.46	0.1
Br	0.010	1.3	0.62	0.1
Rb	0.011	1.4	1.08	0.2
Sr	0.018	2.3	1.23	0.3
Y	0.017	2.1		0.3
Zr	0.021	2.6	2.00	0.6
Mo	0.028	3.5		3.3
Pd	0.058	7.21	Note: In typical	
Ag,Cd	0.061	7.64	amples, interferences	
Sn,Sb,I	0.109	13.60	limit sensitivity.	
Ba	0.675	84.00		1.0
La	0.412	51.30	Note: As above for RE	
Hg	0.028	3.54		0.5
Pb	0.032	3.96	2.00	0.6

Table 8 compares two S-XRF analysis runs on the same DRUM strip, showing that the comparisons of the two runs are excellent for 28 major and minor elements ($\chi^2/\text{point} = 0.57$) and that our sensitivities and quoted uncertainties are realistic.

In May, 2001, this facility was transferred to DELTA Group control at the Dept. of Applied Science, UC Davis, primarily for aerosol work.

Table 8 Comparison of Two S-XRF Analysis Runs on the Same DRUM Strip

UC Davis DELTA Group

Quality assurance tests - Tom Cahill, Steve Cliff, Michael Jimenez-Cruz, March 24, 2002

Synchrotron - XRF analysis of Fresno DRUM strips

March 10 - April 25, 2001, Stage 8 - 0.26 to 0.09 micrometers diameter

July 2001 S- XRF 160 measurements (6 hr steps); January 2002 S-XRF 320 measurements (3 hr steps)

Analysis Run	Na ng/m ³	Mg ng/m ³	Al ng/m ³	Si ng/m ³	P ng/m ³	S ng/m ³	Cl ng/m ³	K ng/m ³	Ca ng/m ³	Ti ng/m ³	V ng/m ³	Cr ng/m ³	Mn ng/m ³	Fe ng/m ³
July, 2001	3.87	0.11	4.42	6.45	4.39	56.57	1.25	10.05	1.15	0.05	0.08	0.08	0.07	1.14
January, 2002	3.42	0.07	2.42	6.56	4.02	54.70	1.15	10.65	0.67	0.05	0.09	0.07	0.09	1.52
average value	3.65	0.09	3.42	6.50	4.21	55.63	1.20	10.35	0.91	0.05	0.08	0.07	0.08	1.33
avg uncertainty in quadrature	2.17	1.02	1.04	1.31	1.10	8.06	0.26	1.49	0.58	0.07	0.06	0.03	0.03	0.24
Measures of Performance														
1. chi-square avg chi sqr	0.04 0.57	0.00	3.73	0.01	0.11	0.05	0.13	0.16	0.68	0.00	0.01	0.27	0.37	2.52
2. Mean error in percent	12.30 5.5 %	39.49	58.41	-1.74	8.74	3.37	7.70	-5.74	52.28	-8.21	-5.35	17.92	-21.40	-29.11

Fe ng/m ³	Co ng/m ³	Ni ng/m ³	Cu ng/m ³	Zn ng/m ³	Ga ng/m ³	As ng/m ³	Se ng/m ³	Br ng/m ³	Rb ng/m ³	Sr ng/m ³	Y ng/m ³	Zr ng/m ³	Mo ng/m ³	Pb ng/m ³
1.14	0.02	0.05	0.07	1.02	0.03	0.05	0.08	0.27	0.00	0.01	0.03	0.06	0.25	0.17
1.52	0.01	0.04	0.09	1.60	0.00	0.11	0.12	0.31	0.01	0.03	0.04	0.08	0.29	0.30
1.33	0.02	0.04	0.08	1.31	0.02	0.08	0.10	0.29	0.01	0.02	0.03	0.07	0.27	0.24
0.24	0.02	0.03	0.03	0.24	0.02	0.17	0.08	0.18	0.10	0.13	0.13	0.15	0.31	1.07
2.52	0.16	0.09	0.53	5.80	0.86	0.12	0.18	0.05	0.01	0.01	0.01	0.01	0.02	0.01
-29.11	50.70	18.85	-30.32	-43.67	136.92	-74.24	-33.49	-14.01	-99.78	-67.35	-36.78	-18.62	-16.53	-53.73

The switch from the 1 liter/min jetted DRUM (1985) to the 10 liter/min slotted DRUM (MSAM 1992, DELTA DRUM 1999) improved precision for major elements from about 15% to about 5% for both PIXE and S-XRF. But returning to the example above in Section 5, with S-XRF we roughly maintain the same cost/strip, \$1,200. but achieve improved capabilities:

	PIXE	S-XRF
Time resolution	2 mm = 12 hrs	0.5 mm = 3 hrs
MDL	30 ng/m ³	0.1 ng/m ³

For the example quoted, S-XRF would deliver 2,720 individual S-XRF analyses at an average cost of \$3.25/analysis, delivering an average (ACE-Asia) of 30 elements/analysis, plus many upper limits of elements not seen (mainly in the silver through rare earths region). Data handling becomes a serious problem with 75,000 to 90,000 measurements for each 6 weeks period.

Table 9 Comparison of Analytical Techniques from the Charleston EPA/DOE Inter-comparison (Cahill, 1980)

Method by type	# of Groups reporting	Solution standards	Rock standards	Aerosol standards	Aerosol samples
PIXE	7	1.03 ± 0.16	0.99 ± 0.29	0.99 ± 0.19	0.99 ± 0.07
ED - XRF	8	0.97 ± 0.12	1.07 ± 0.20	1.03 ± 0.14	1.02 ± 0.09
λ - XRF	3	1.19 ± 0.34	1.12 ± 0.47	1.37 ± 0.50	na
AA, ES	3	0.88 ± 0.17	0.40 ± 0.31	0.47 ± 0.29	na
NAA	1	0.97 ± 0.08	na	na	na

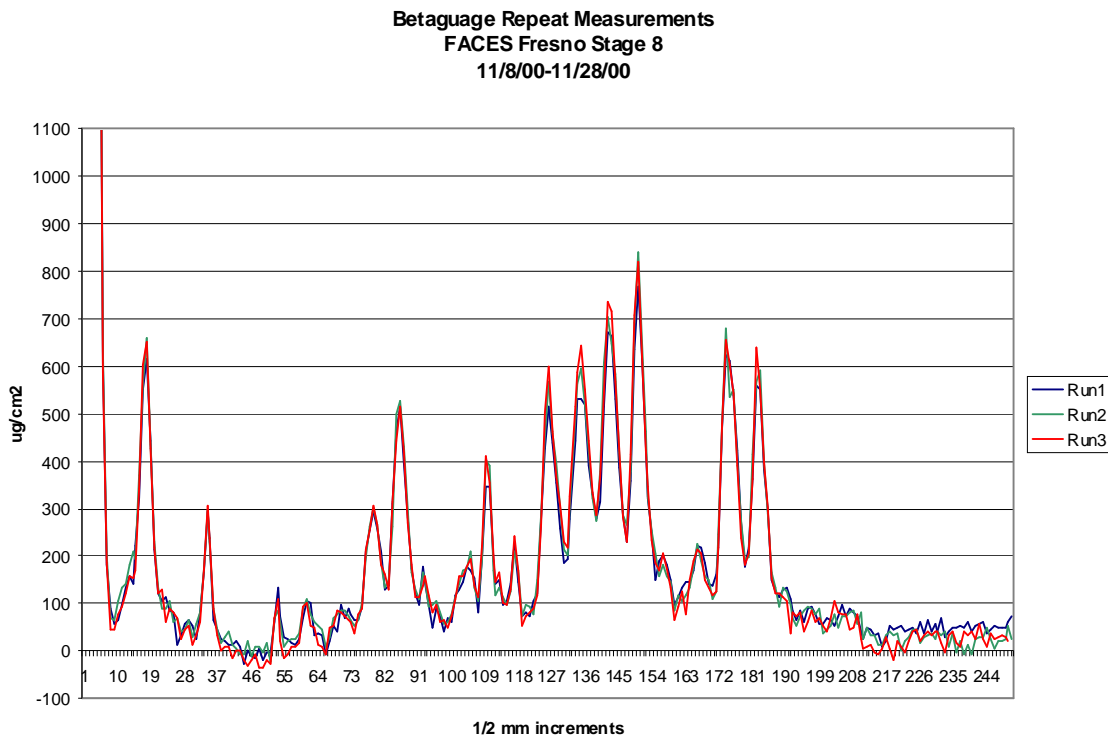
Based on other tests, we find that neutron activation analysis (NAA) is essentially identical with the x-ray methods, especially the energy dispersive (ED) techniques PIXE and ED-XRF. This same problem was observed in the recent NSF-funded ACE-Asia study. A set of loess standards were circulated to investigators, and those using standard extraction techniques such as EPA Method 3052 digestion and detection by ICP/MS tended to be low (Appendix G), averaging 0.74 ± 0.22 of the standard, with some elements as low as 0.345. Note that we and most other XRF groups have obtained NIST SRMs that are essentially identical to the aerosols sample on an as-is basis, difficult or impossible for extraction-based techniques. Thus, great caution must be exercised in comparing analytical and sampling techniques on actual aerosol samples if one involves an extraction protocol.

Section 4.09 Soft Beta Mass Analysis (BETA)

Through use of low energy beta particles matched to the impactor strips, mass is obtainable in air and at a very low cost. Figure 4 shows repeated analysis of the same DRUM strip used for the CAMS STIM and PESA work, showing the precision achieved in re-analysis. Automation was completed Winter, 2002, and minimum detectable limits and precision have been established. The MDL depends on a number of factors, but for a relatively clean sample operating at a 6 week rotation rate it is approximately $0.5 \mu\text{g}/\text{m}^3$.

It is the plan to put every DRUM stripped collected through this analysis. Figure 4 shows a soft beta analysis mass of a DELTA 8 DRUM operating in Tango, Japan, as part of the ACE-Asia program.

Figure 2 Precision of Mass by Betagauge through Repeated Measurements of a DRUM Strip.



Section 4.10 Wavelength Resolved Optical Extinction.

We have found dramatic differences in aerosol color once the samples are resolved in size and time. These will also be routinely recorded in the range 320 nm (set by an absorption band in Mylar) to 820 nm. Figure 5 shows optical data on the on a 8 stage DELTA DRUM sampler used above in Figure 4 for soft beta mass at Tango, Japan.

To understand the behavior of the absorption coefficient, we are spectrally measuring the attenuation of a white light through a deposited PM sample on mylar. A solarization resistant fiber with a 300 μm core is attached to an Ocean Optics Mini-D2T Deuterium Tungsten Halogen Light Source (~200-1100 nm). The bare fiber is placed on one side of the sample, approximately 2 mm from the mylar strip. The transmitted light is collected and measured by an Ocean Optics USB2000 fiber optic spectrometer terminated with a collimating lens, approximately 5 mm from the source fiber. The spectrometer has 2048 channels covering a spectral range of ~200 nm-1100 nm.

The combination of the light source and the spectrometer system has an effective spectral range of 200 nm-850 nm with a 2 nm resolution. Mylar transmits 65%-80% of light at wavelengths greater than 325 nm. This falls off more than four orders of magnitude by

300 nm. We have found that the longest usable wavelength is in the range of 800 nm-820 nm. By scanning across the fiber in 50 μm steps, we have demonstrated that we are only sensitive to directly transmitted light over dimensions approximately equal to the 300 μm core diameter. The measurements are insensitive to scattered and stray light.

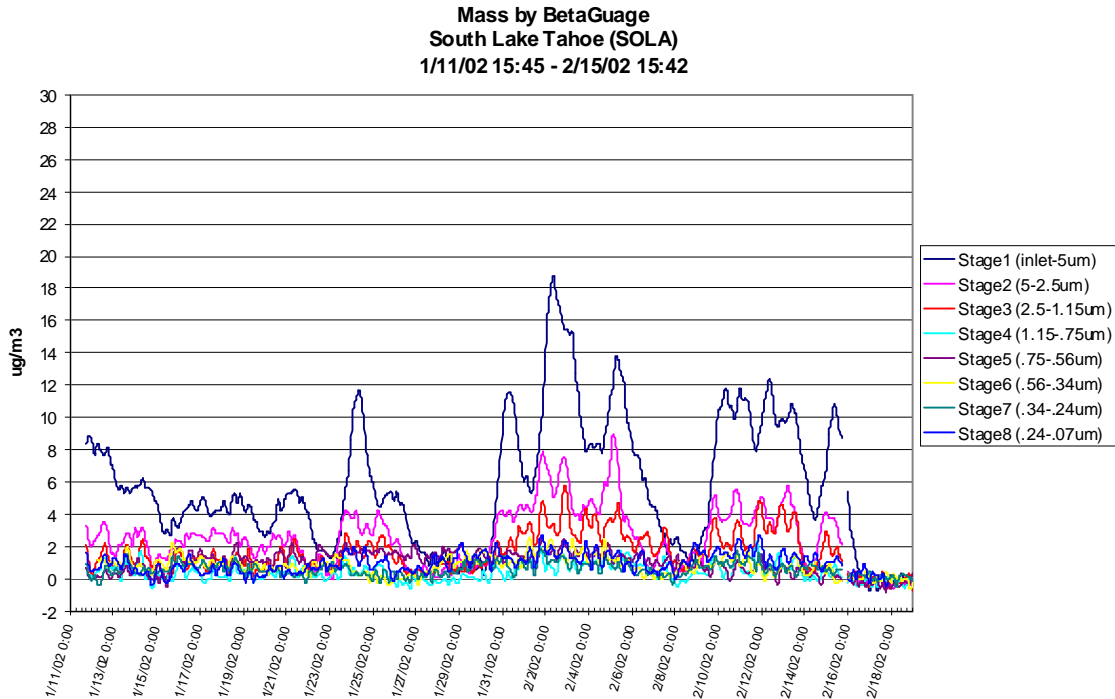
Forward attenuation at a wavelength λ is reported as:

$$FA(\lambda) = -\ln\left(\frac{I(\lambda) - D(\lambda)}{I_0(\lambda) - D(\lambda)}\right)$$

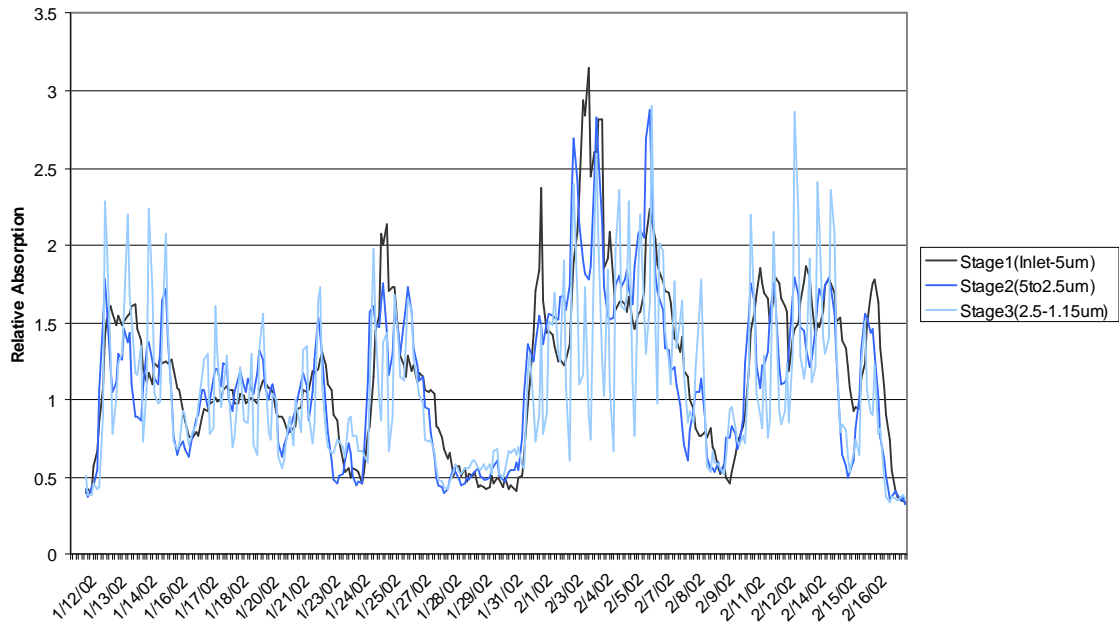
where *FA* is the forward attenuation, *I* is the intensity through a deposited PM sample, *I*₀ is the intensity through clean greased mylar, and *D* is the dark current (light source blocked) measurement.

Because of the enormous amount of data generated by the optical analysis at its normal 0.25 nm resolution, (30 Gb/6 week 8 DRUM), and with knowledge of the natural phonon broadening in solids, we have as a first trial averaged over 40 nm bits, giving 11 bite spectra every 3 hours for every stage. Below we show the results for mass be soft beta gauge and optical attenuation in the uv - 320 - 260 nm, taken at South Lake Tahoe, January - February, 2002.

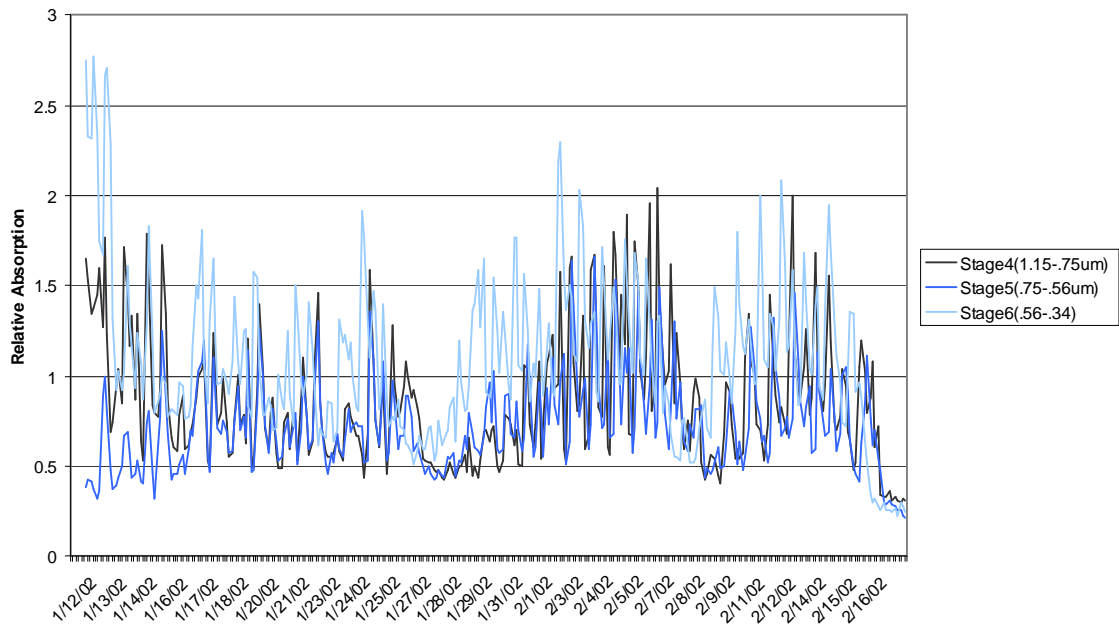
Figure 3 Comparison of Mass and Optical Attenuation from DRUM Strips at South Lake Tahoe, CA.



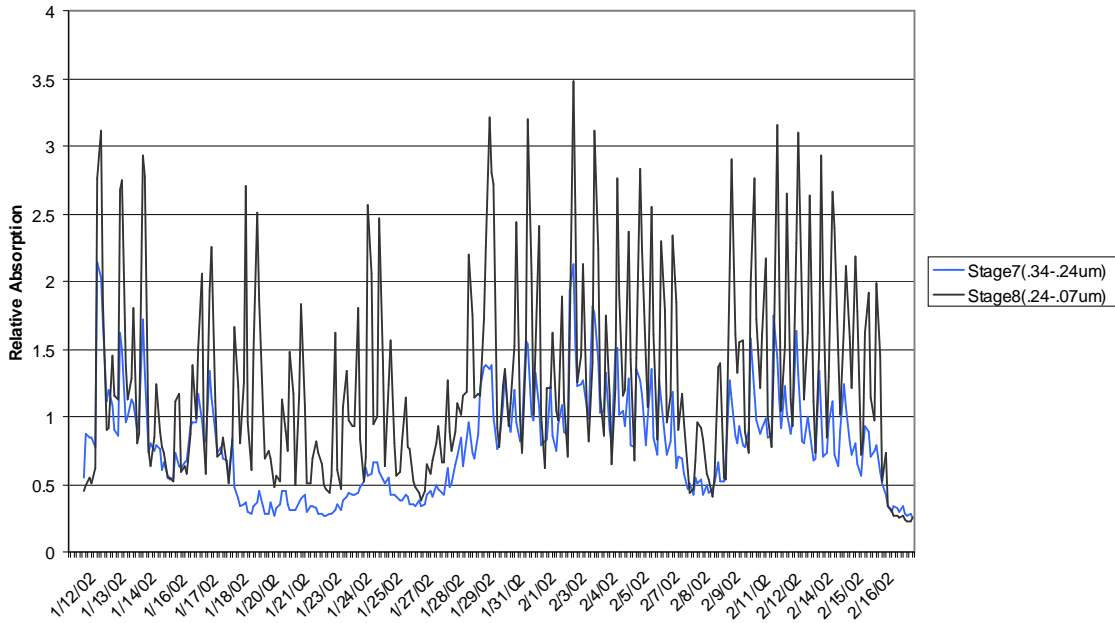
320 to 360 nm
South Lake Tahoe, NV
1/11/02 15:45 - 2/15/02 15:42



320 to 360 nm
South Lake Tahoe, NV
1/11/02 15:45 - 2/15/02 15:42



320 to 360 nm
South Lake Tahoe, NV
1/11/02 15:45 - 2/15/02 15:42



Note that the attenuation per unit mass is 10 times greater in the 0.26 to 0.09 micron stage, dominated by highly absorbing very fine aerosols (not wood smoke).

Article V. These two techniques are inexpensive, together circa \$200./strip or, for a 3 DRUM on a 6 week rotation rate and using 3 hr time resolution, under \$6,000./year for both techniques together. Validation - Level 0 & 1 for the DELTA Group 8 DRUM

Article VI. Validation Level 2 Versus Other Laboratories

Section 6.01 Comparison to Filters

The first step in Level 2 validations of the DRUM sampler is to separate the sampling factors from analytical factors. In this regard, previously analyzed filters from other groups using non-destructive techniques allows for analytical comparisons without sampling factors included. Two such inter-comparisons have recently been concluded; IMPROVE BRAVO filters (6) from the EPA BRAVO study of 1999, and CARB Dichot filters (6) from the CARB FACES study of 2001, and

(a) Comparison with IMPROVE Filters

The accuracy of S-XRF was recently validated through a blind inter-comparison with IMPROVE as part of the EPA/NPS BRAVO Study in Big Bend NP, Texas (Appendix F). The analyses showed (see example of one filter, below):

- 1. **Ratio IMPROVE PIXE/DELTA S-XRF Al, Si, S, K, Ca, Fe** **0.99 +/- 0.04**
- 2. **Ratio IMPROVE XRF/DELTA S-XRF Cu, Zn, Br, Sr, Pb** **1.24 +/- 0.14**

In the latter samples, it was detected that the PIXE analysis had caused sample loss which made the IMPROVE XRF values slightly higher

- 3. Mean MDL, IMPROVE PIXE.DELTA S-XRF x 48
- 4. Mean MDL, IMPROVE XRF/DELTA S-XRF x 2

This latter value was exactly what was predicted, S-XRF twice as good as IMPROVE XRF, and agrees with the quoted S-XRF values for a 30 second S-XRF run versus 800 sec IMPROVE XRF run (see Appendix D).

The fact that the comparison between IMPROVE’s x-ray methods (PIXE, XRF) and DELTA’s synchrotron XRF are very good simply confirms earlier work that all x-ray methods tend to be accurate. The reason is most likely tied to the fact that the filters are analyzed on an as-is basis, filter plus deposit, rather than being removed from the filter, digested in acids, or other such process.

This was shown above in Table 9 where we reproduced data from an EPA/DOE inter-comparison in Charleston, West Virginia, in 1978. All groups do a good job on the solution standards, deposited drop by drop on Whatman 41 cellulose filter paper. However, the techniques that rely on fluid extraction (atomic absorption AA, emission spectroscopy ES) were highly variable, with some elements (such as zinc and lead) being correct and others (including alumino-silicates) being as much as an order of magnitude low.

There were a few minor elements in which there were gross disagreements, often between CNL PIXE and CNL XRF in the overlap region. Since the S-XRF results were the average of between 10 and 16 independent measurements, we believe that on that basis plus the vastly superior MDLs, the S-XRF data are more credible.

Table 10 Blind Filter Inter-Comparison with IMPROVE at the EPA BRAVO Study

Avg MDLs	Avg MDLs	Avg MDLs	Avg MDLs	BRAVO BR2, Oct 4			BRAVO BR4 Octr 22		
CNL PIXE+XRF	CNL MDL PIXE+XRF	DELTA S-XRF	DELTA S-XRF	CNL PIXE + XRF	DELTA S-XRF average 16 points	DELTA error	CNL PIXE+XRF	DELTA S-XRF average 10 points	DELTA Std
Element (Switch at Fe)		Element							
pna	147.6	Na	8.8	2504	979	208.8	0	18	20
pmg	84.9	Mg	7.0	0	300	141.4	0	111	35
pal	47.8	Al	3.1	1675	2050	249.9	442	580	57
psi	37.6	Si	1.6	4474	4720	500.5	1336	1329	106
pp	34.1	P	1.0	0	812	79.6	0	277	15

ps	33.4	S	1.3	14511	15971	1574	3955	4316	294
pcl	32.4	Cl	0.4	0	55	12.8	0	18	2
pk	22.4	K	0.3	711	740	85.0	268	291	20
pca	17.5	Ca	0.3	2360	2417	240.5	872	821	103
pti	17.1	Ti	0.9	146	170	28.9	34.7	45.1	7.5
pv	0.3	V	0.2	10	18	7.3	0.5	2.2	2.9
pcr	11.3	Cr	0.1	47	2	1.0	12.5	0.6	0.6
pmn	11.5	Mn	0.1	30	24	10.1	17.9	8.2	4.4
fe	2.0	Fe	0.2	1040.3	994.7	131.5	387.6	472.4	531.5
co	na	Co	0.2	0	6.5	1.2	0	4.2	3.1
ni	1.6	Ni	0.2	0	50.0	9.8	0	4.1	1.6
cu	1.2	Cu	0.3	0	12.0	2.4	0	2.8	0.8
zn	0.8	Zn	0.2	25.1	29.8	5.2	8.9	9.9	2.1
ga	0.6	Ga	0.2	0	0.2	0.3	0	0.3	0.2
as	0.5	As	0.4	4.4	2.0	3.6	0	1.1	1.1
se	0.6	Se	0.3	4.5	2.1	1.6	0	1.2	0.7
br	0.6	Br	0.4	32.0	12.6	3.4	16.9	7.7	0.9
rb	1.0	Rb	0.6	0	1.3	2.2	0	1.3	1.3
sr	1.0	Sr	0.7	10.0	5.3	5.4	2.3	0.9	0.9
y	1.2	Y	0.9	0	2.0	2.7	0	0.5	0.8
zr	1.6	Zr	1.2	0	2.9	3.3	0	1.5	2.5
		Mo	1.5		9.2	8.5	0	4.8	7.5
pb	1.1	Pb	1.7	4.2	11.7	15.9	0	3.9	4.8

(b) Direct Comparison with CARB Dichot Filters Analyzed by XRF, and Indirect Comparison with ARB RAAS Results (ICP/MS)

The inter-comparison of filters between ARB and DELTA Group has always been a critical part of the quality assurance program as it allows separation of effects associated with the analytical methods (XRF and ICP/MS ARB, versus S-XRF DELTA Group) from effects associated with sampling protocols (DELTA Group DRUM impactor sampling versus ARB Dichot and RAAS filter sampling).

In May, 2002, we received from the ARB the Dichot filters for PM10 and PM2.5 for the dates March 14, 23, April 1, 7, 13, and 19, 2001, all taken at the ARB Fresno First Street site. (314C, 314F, 323C, 323F, 401C, 401F, 407C, 407F, 413C, 413F, 419C, 419F). The deposit diameter was measured (essential for conversion to ng/m^3) and the filters were sectioned using a new Stainless steel surgeon's scalpel on an alcohol washed Teflon cutting board into 2 halves, one of which was retained in the original Petri dishes, the other mounted in an aluminum filter frame for S-XRF analysis. The analyses were done on June xx, 2002, at the DELTA Group "white" S-XRF facility at Beam Line 10.3.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory (for details see the DQAP7.02). After full QA procedures were completed, including a high quality smooth fit to all 65 NIST traceable elemental standards (DQAP7.02, Appendix H), five locations were sampled on each filter, and the results summed to provide an average value. The results were corrected for particle size effects (see DQAP7.02, Appendix D), converted to areal density using the measured filter area and the air volume provided with the filters.

(c) Results

During 6 of the sampling periods, data were available from all three filter samplers for four elements Mn, Fe, Zn, and Pb. These are shown below, with the values in ng/m^3 . The Mn, Fe, Zn, Pb LODs are as quoted by the ARB, the value next to the DELTA S-XRF data are total propagated errors. Note that the DELTA S-XRF analyses were directly compared to the Dichot filters, as those were the same physical filters analyzed by both groups.

The ARB RAAS data were not accompanied with level of detection, minimum detectable limits, errors, or corrections, indicating that this may be a technique under development by the CARB. In this situation, it is hoped that this inter-comparison can assist CARB in improving their data, probably through more complex extraction techniques.

Table 11 Results of Comparisons with CARB Filters and RAAS Data.

DELTA - ARB Filter comparison			Mn	Mn LOD	Fe	Fe LOD	Zn	Zn LOD	Pb	Pb LOD
March	14	ARB Dicot	2	1	97	1	10	1	4	2
		ARB RAAS	1.96		108		7.28		1.74	
		DELTA Dichot	2.18	0.406	109.88	7.986	10.26	1.073	0	9.952
	23	ARB Dicot	0.5	1	42	1	16	1	3	2
		ARB RAAS	1.5		49.8		17.1		1.03	
		DELTA Dichot	1.07	0.307	56.39	4.22	18.07	1.645	0	8.538
April	1	ARB Dicot	2	1	88	1	12	1	4	2
		ARB RAAS	2.08		82.6		8.91		0.81	
		DELTA Dichot	2.09	0.411	88.02	6.451	11.06	1.125	0	9.098
	7	ARB Dicot	0.5	1	21	1	4	1	1	2
		ARB RAAS	0.24		22.9		0.92		0.11	
		DELTA Dichot	0.52	0.217	21.93	1.799	3.55	0.58	0	8.609
	13	ARB Dicot	2	1	57	1	21	1	2	2
		ARB RAAS	3.34		63		18.8		1.73	
		DELTA Dichot	1.39	0.31	62.56	4.651	20.16	1.789	0	9.502
	19	ARB Dicot	4	1	147	1	5	1	1	2
		ARB RAAS	2.08		98.8		3.93		2.66	
		DELTA Dichot	3.78	0.532	169.71	12.189	4.94	0.666	0	8.405

We will focus on this part of the summary those data for which all measurements by all groups were above LODs or total errors. This eliminates S-XRF lead values for this comparison.

In summary, there was excellent agreement between ARB Dichot and DELTA S-XRF Dichot analyses:

Ratio 1.02 ± 0.11 , 16 measurements, with the minimum ratio 0.7 and the maximum ratio 1.7.

However, ARB Dichot and ARB RAAS data had much poorer inter-comparison,

Ratio 1.29 ± 0.63 , 16 measurement, with the minimum ratio 0.6 and the maximum 4.35.

as did the DELTA S-XRF Dichot and the ARB RAAS,

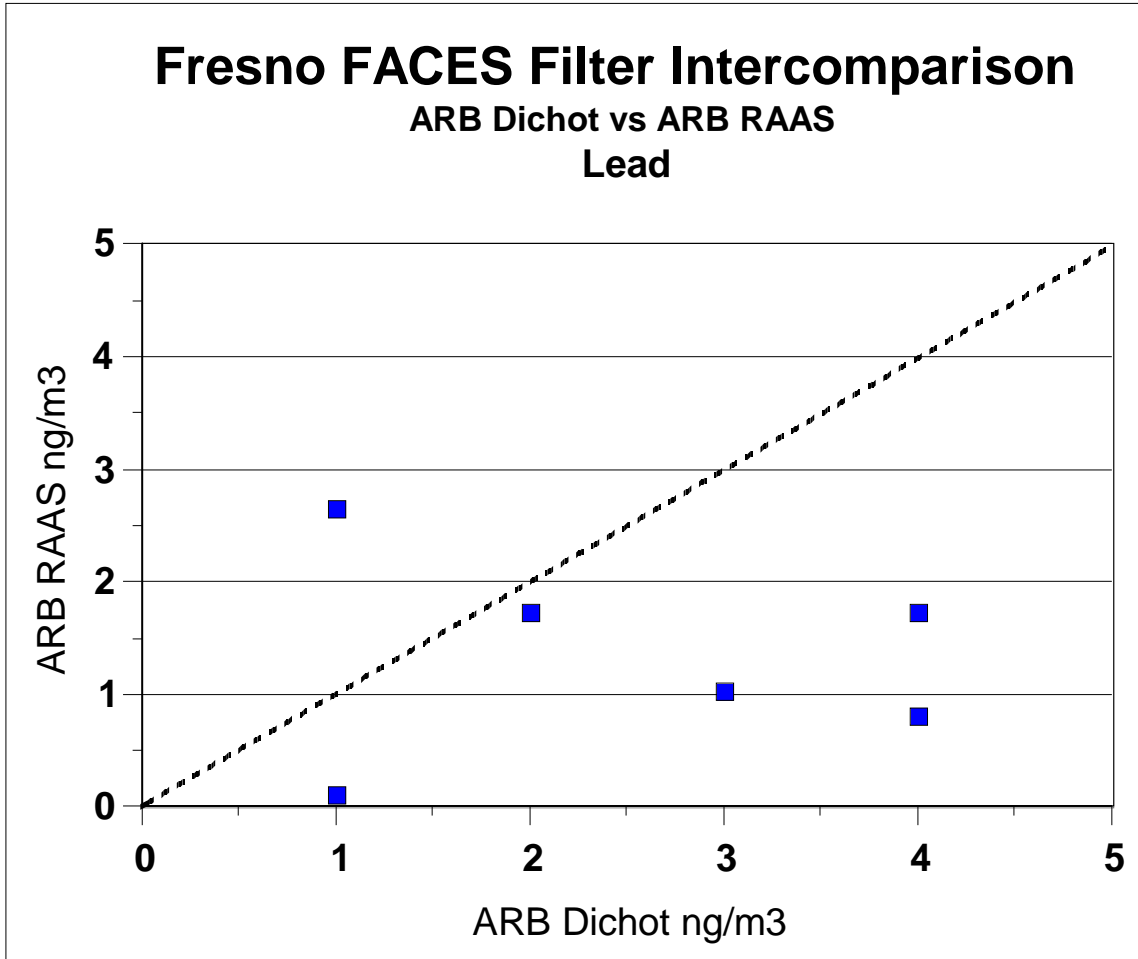
Ratio 1.29 ± 0.58 , 16 measurements, with the minimum ratio 0.42 and the maximum 3.86.

The comparison of ARB Dichot to ARB RAAS for lead was poor,

Ratio 2.83 ± 1.37 , 4 measurements, with the minimum ratio 1.16 and the maximum 4.94.

These data are plotted below. The one to one line is plotted in each case. It is not a fit to the data.

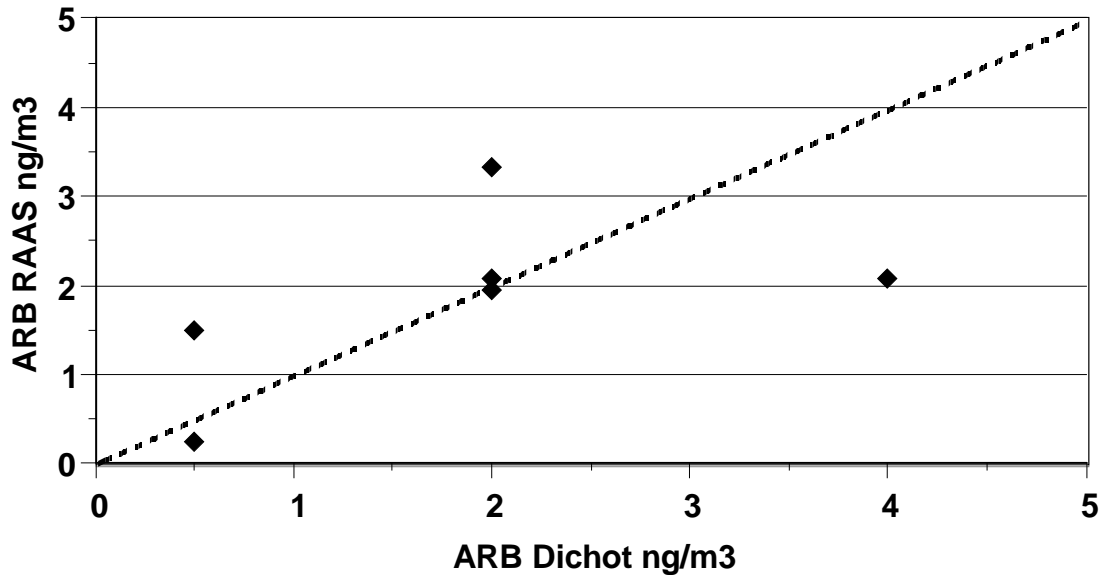
Figure 4 (a-d) Filter-to-Filter comparisons to CARB Data.



Fresno FACES Filter Intercomparison

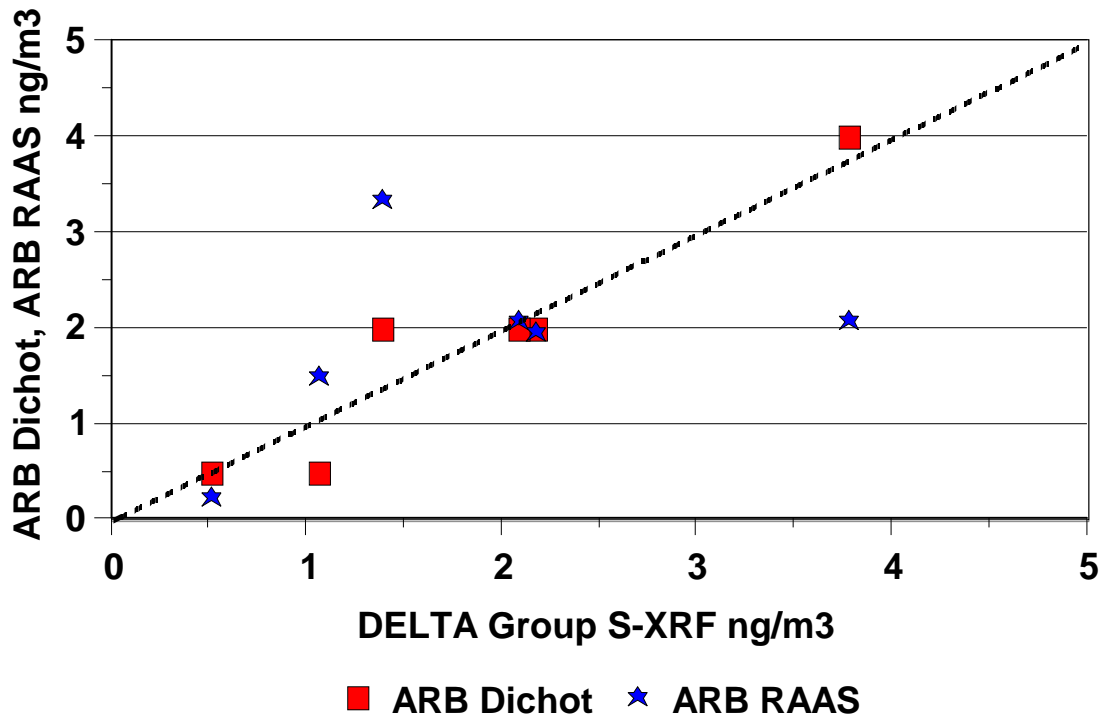
ARB Dichot vs ARB RAAS

Manganese



DELTA S-XRF vs ARB Dichot and ARB RAAS Filters

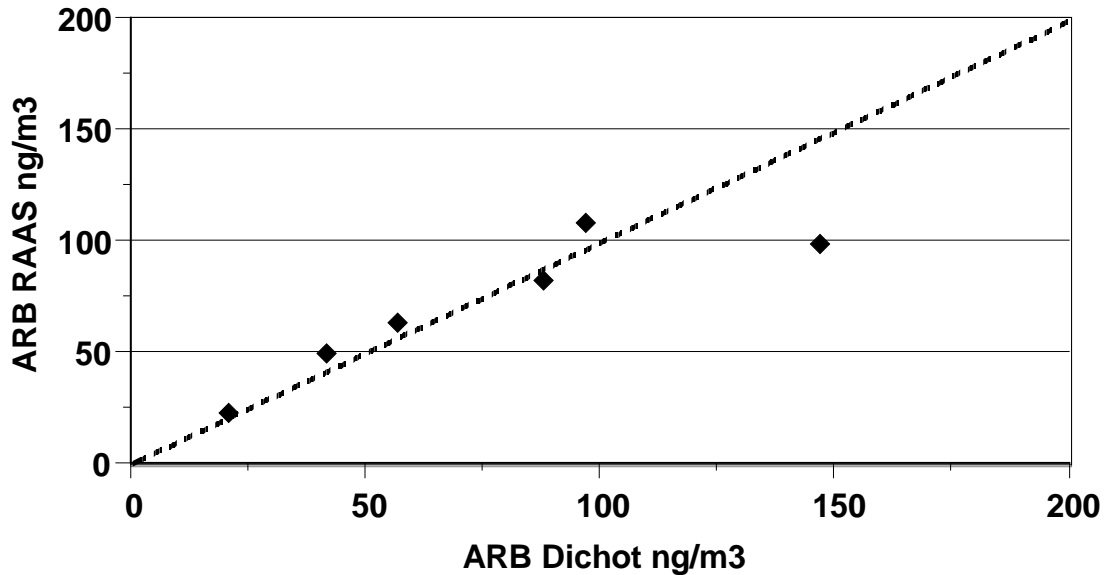
Manganese



Fresno FACES Filter Intercomparison

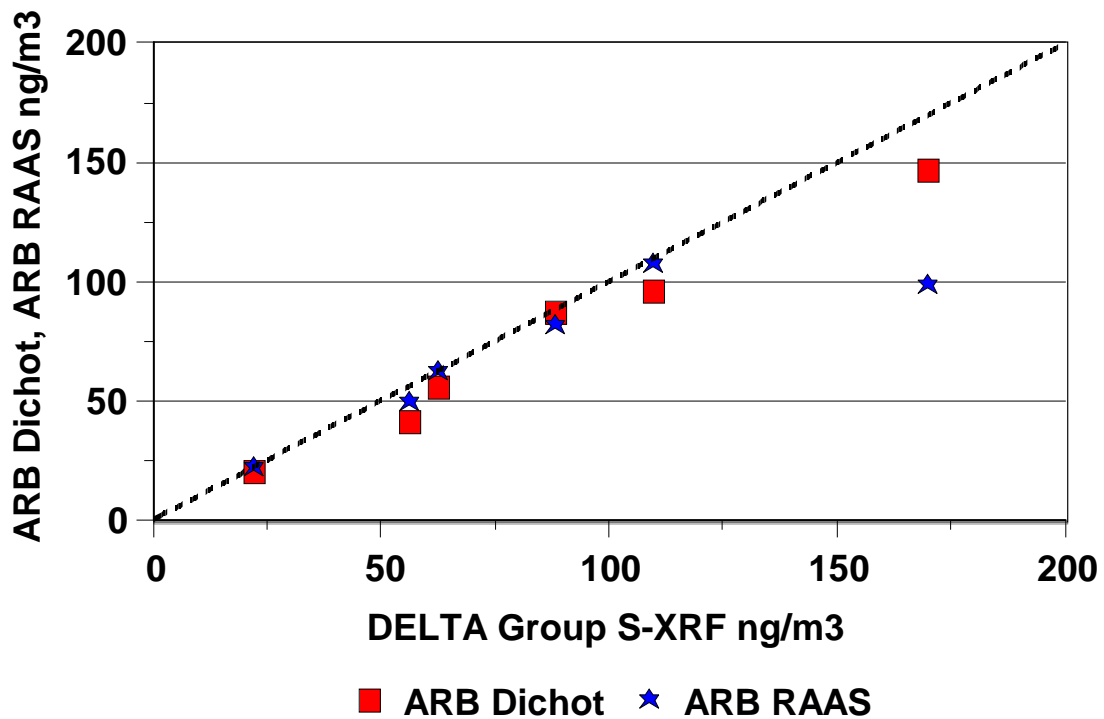
ARB Dichot vs ARB RAAS

Iron



DELTA S-XRF vs ARB Dichot and ARB RAAS Filters

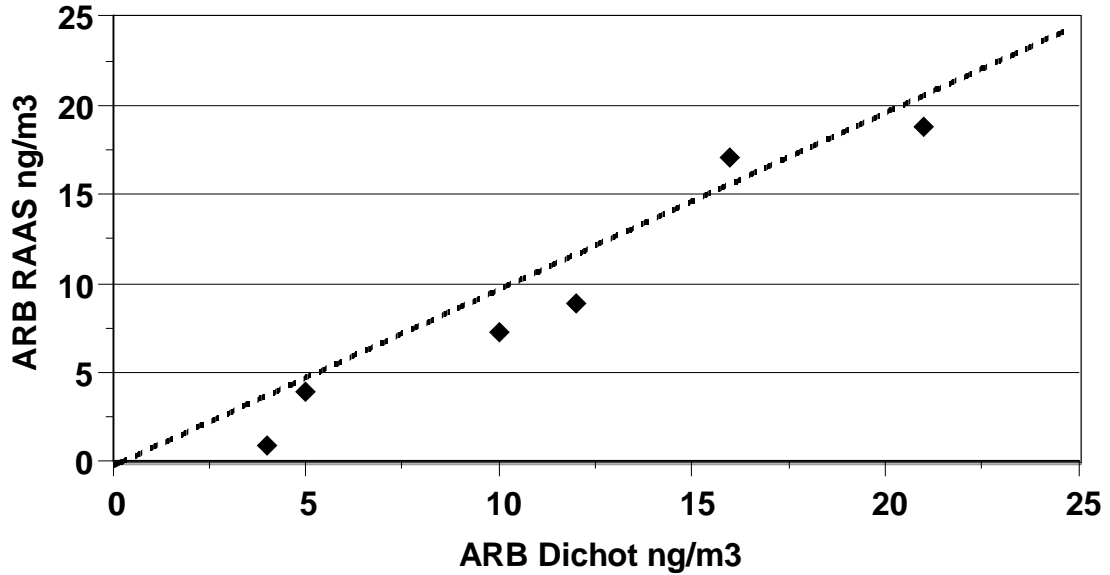
Iron



Fresno FACES Filter Intercomparison

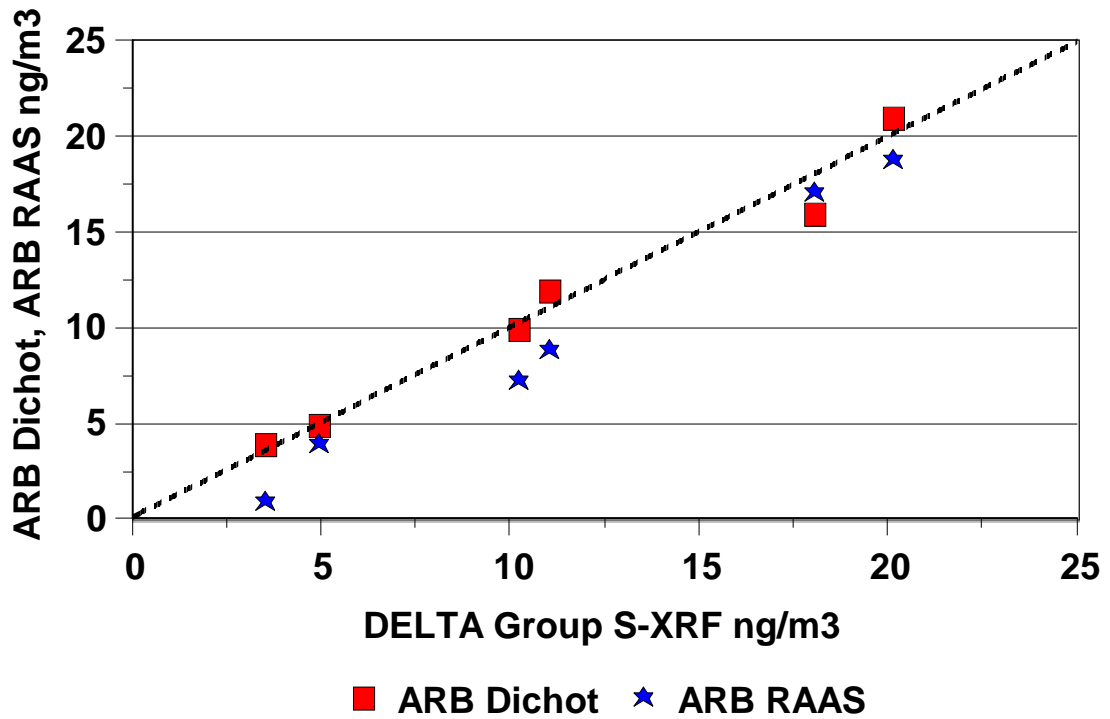
ARB Dichot vs ARB RAAS

Zinc



DELTA S-XRF vs ARB Dichot and ARB RAAS Filters

Zinc



(d) Interpretation

It is clear from these data that the DELTA S-XRF and ARB Dichot measurements are in excellent agreement, echoing prior work over the past 20 years and other tests done this Spring in a blind comparison with IMPROVE Teflon filters, 0.99 ± 0.04 , Na to Fe (DQAP7.02). This agreement for the ARB Dichot filters occurred despite extensive handling of the filters, different areas of analysis, and other factors, any one of which could make the agreement poorer.

It is also clear from these data that the two ARB derived values are in severe disagreement even for these abundant and well studied elements, using data that have been in the hands of the ARB since at least December, 2001. The nature of the disagreement provides valuable information on the sources of the error. The manganese data for ARB Dichot vs. ARB RAAS are consistent with either a statistical uncertainty of either roughly $\pm 50\%$ or $\pm 1 \text{ ng/m}^3$ or random systematic errors. The iron data for ARB Dichot vs. ARB RAAS are consistent with a statistically robust measurement for the lowest values (1.03 ± 0.06 in the ratio, or about $\pm 3 \text{ ng/m}^3$), but that makes the ratio of 1.72 wildly improbable. The error of 48 ng/m^3 is 8 standard errors, or a probability $\ll 0.001$ by the Method of Maximum Likelihood (Bevington, 1969) as being part of the same statistical set. Thus, we must assume a serious systematic error in the ARB RAAS data for the highest compared value of iron. This same situation occurs for the lowest measured value of zinc, (3.6 ARB Dichot vs 0.9 ARB RAAS) but this could be consistent with either a statistical uncertainty of $\pm 2.5 \text{ bg/m}^3$ of a systematic error of 3.8 in the ratio. Similar conclusions can be made for the ARB Dichot lead vs. ARB RAAS lead values. In summary, it appears that for these major and minor elements, all relatively abundant, the ARB RAAS data has serious systematic errors, perhaps compounded by statistical and/or minimum detectable limit problems.

The situation is made more serious by what appears to be inconsistencies of the ARB RAAS data with prior published ARB work at Fresno (Chow et al 1994). For example, in the present tests, the ARB RAAS measured values of gallium on 4 of the 6 days, with amounts 5.2 ng/m^3 (3/14), 1.5 ng/m^3 (4/01), 1.6 ng/m^3 (4/07) and 4.4 ng/m^3 (4/19). Yet Chow et al. never observed gallium in 35 prior measurements at the same site in Fresno, with a level of detection of 0.5 ng/m^3 , leading to the conclusion that the average gallium level at Fresno has to be much less than 0.25 ng/m^3 . Note that the S-XRF results on the Dichot filters never showed gallium at a level of 0.3 ng/m^3 . Similar discrepancies occur with other minor and trace elements. Either there have been major changes in the air of Fresno, including a new and unsuspected gallium source, or the ARB RAAS data can be in error by as much as an order of magnitude, perhaps more.

The difficulty in extracting materials from an air filter into solution have been extensively documented, including recent data from NSF-ACE Asia, Prof. Richard Arimoto, U. New Mexico, included in DQAP7.02, Appendix G. This study showed that even EPA Digestion Protocol 3052 was unable to bring most elements in a loess aerosol standard into solution for ICP/MS analysis, reporting errors as high as a factor of 3 in both directions.

The conclusion, supported by other more extensive tests and wider elemental ranges (DQAP7.02), is that DELTA S-XRF measurements on air filters are accurate, precise, and sensitive within the quoted errors and minimum detection limits.

Section 6.02 DRUM Filter Inter-Comparisons

DQAP protocols routinely call for DRUM impactors be run and compared with side-by-side filters, as this has always been an essential part of DELTA Group quality assurance protocols. For the jetted DRUM impactors, such comparisons were done and have been published for the original design (Cahill et al., 1985), the 1986 ARB Carbon Soot-out (Cahill et al., 1990), and for IMPROVE, WHITEX (1991), PREVENT (1992), SEAVS (1995), and MOHAVE (1996). Many of these are summarized in Cahill and Wakabayashi (1993). Of particular interest is the extensive comparison between the jetted DRUM sampler and IMPROVE filters in Shenandoah NP (Cahill et al., 1996). The agreement was excellent for total sulfur, PM_{2.5} versus the sum of DRUM stages, but the DRUM data showed that IMPROVE had seriously misread the chemical composition. IMPROVE routinely reported that the chemical state was ammonium bisulfate, based on 24 hr filters. The DRUM data showed that the chemical state was almost never ammonium bisulfate, but fluctuated from ammonium sulfate at night to highly hydrolyzed sulfuric acid during the day.

For the slotted DRUM impactor, the first comparison to filters (other than the historical data in the period 1973-1979) was the MSAM final report (MSAM 1993).

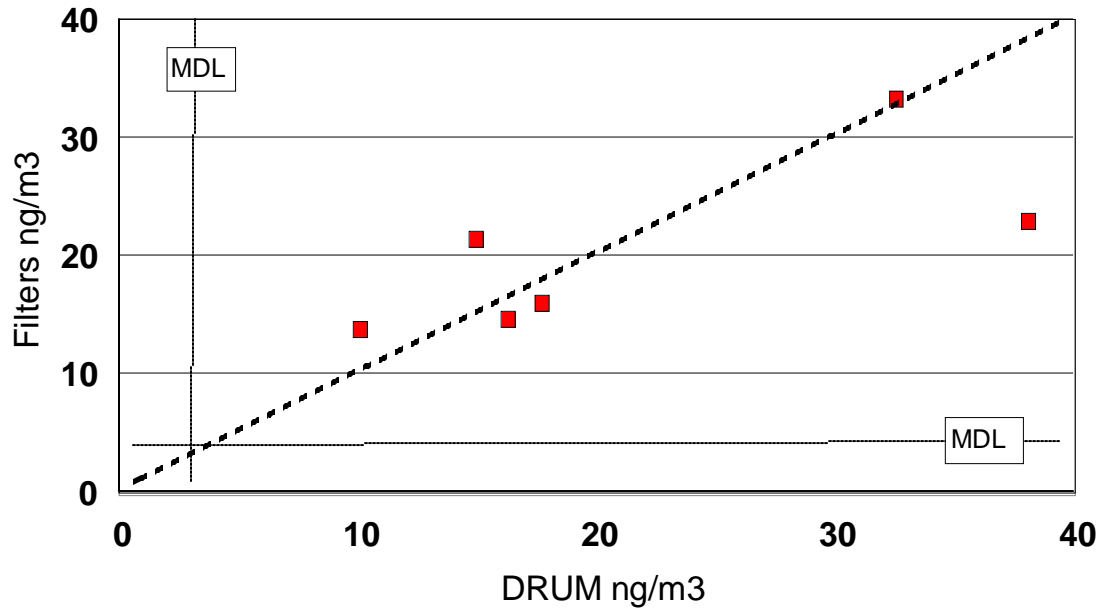
(a) Results of DRUM Filter Inter-comparisons

With the question of analytical equivalence established, we used the same data, namely the ARB Dichotomous filter data analyzed by the ARB (XRF) and the DELTA Group (S-XRF), to compare filters and DRUM data on March 14 and 23, April 1, 7, 13, and 19, 2001. In these data, we used the revised time marked DRUM (corr) that shifted the middle 14 days by 3 hr and the last 14 days by 6 hr. While this made little change in most elements, a few such as zinc had extreme changes in time, and even a small shift in time (6 hr out of 1000) made important changes in daily average concentrations.

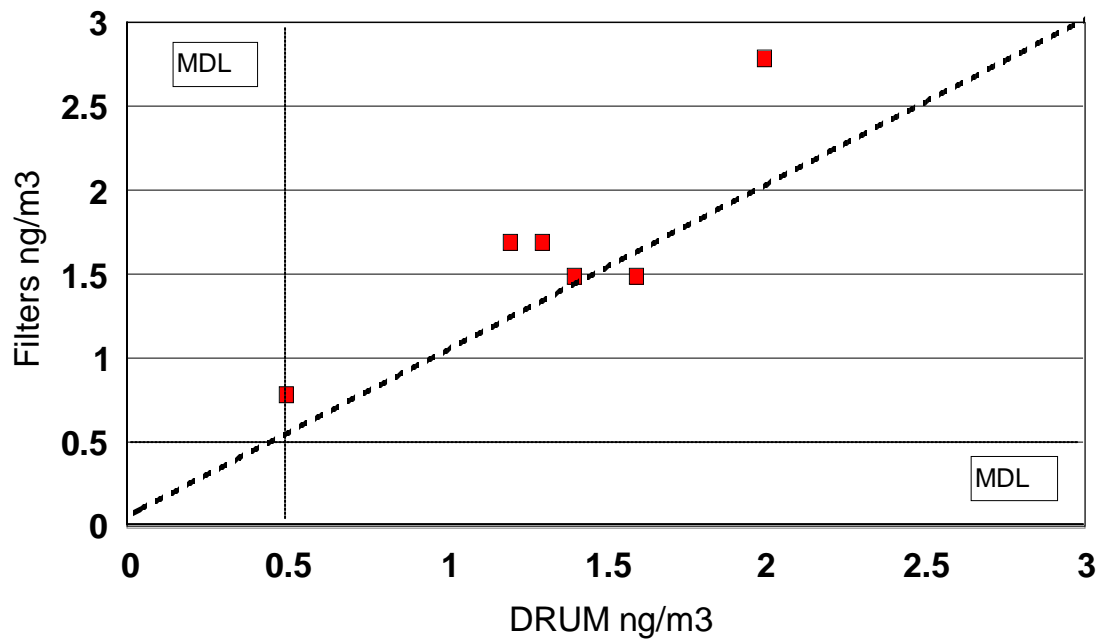
In summary, the agreement between the DRUM and filter (DELTA S-XRF and ARB XRF) data was 0.99 ± 0.40 for the non soil elements Ti, V, Cr, Ni, Cu, Zn, Ga, As, Se, and Pb when both measurements were above MDL. For the large soil derived elements manganese and iron, however, the data were highly correlated but with a value 2.9 ± 0.3 , indicting more soil on the DRUM than the filters. This is, however, what can happen when soil lies at the 2.5 μm cut point. The DRUM sampler, with its sharp cut point, collects soil particles differently than the soft cut point of a virtual impactor or cyclone (including IMPROVE). The efficiency of the DRUM is insured by the grease coating of the stages, a technique almost never used on filters. This provides an excellent reason to use highly size resolved samplers to reduce these uncertainties, un-resolvable with merely a PM₁₀ to PM_{2.5} comparison.

The data used in the comparisons and scatter plots of some of the species are shown below.

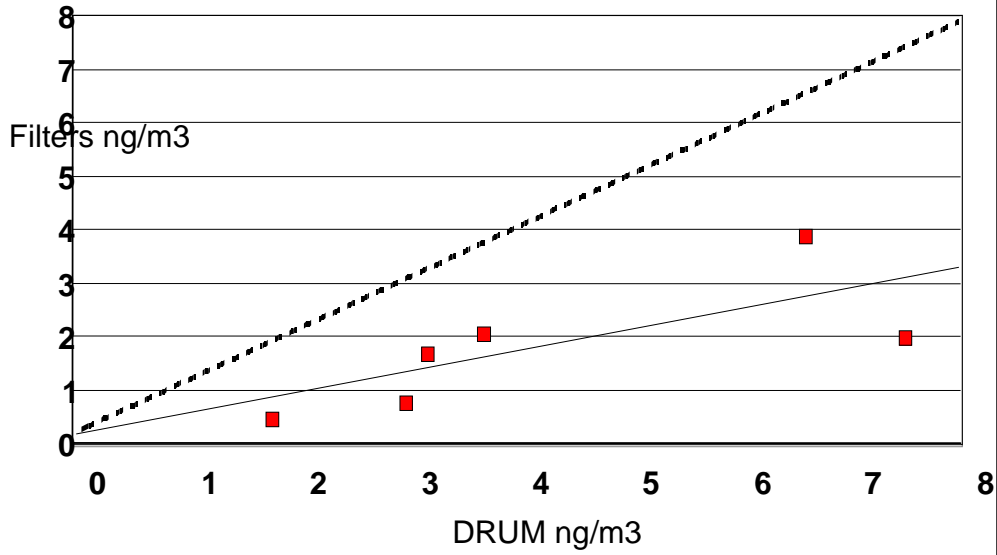
DELTA DRUM vs. ARB Filter Inter-comparison Fresno March-April 2001 Titanium



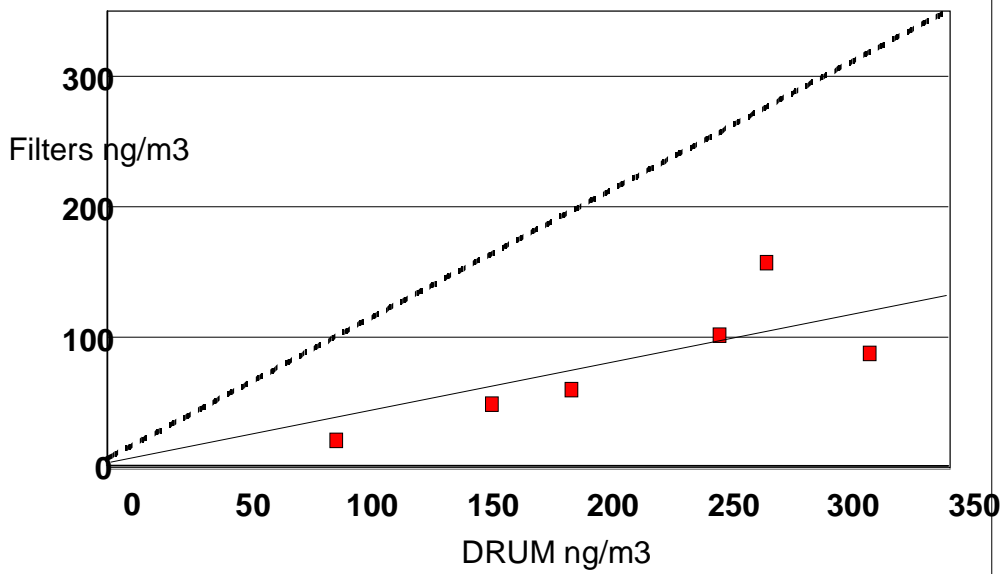
Vanadium



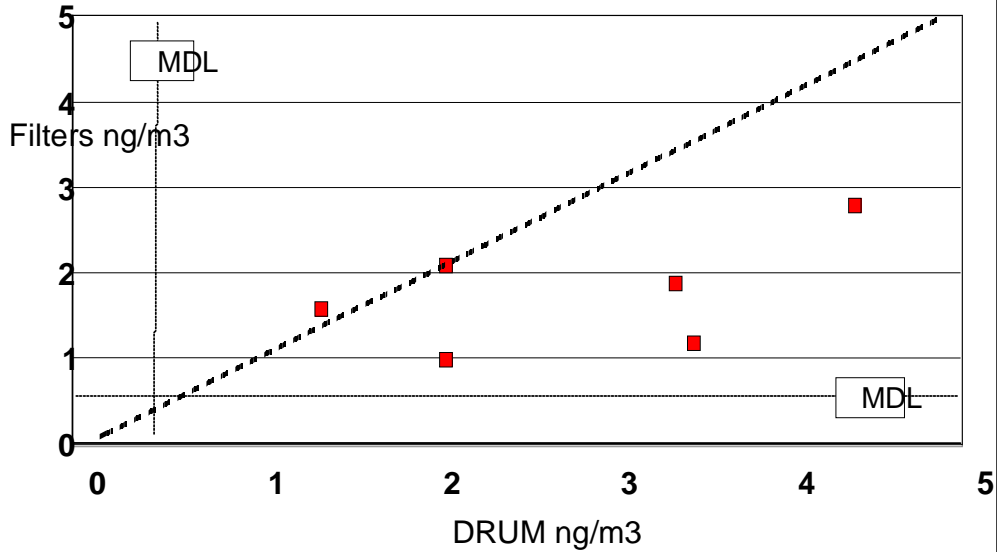
DELTA DRUM vs. ARB Filter Inter-comparison
Fresno March-April 2001
Manganese



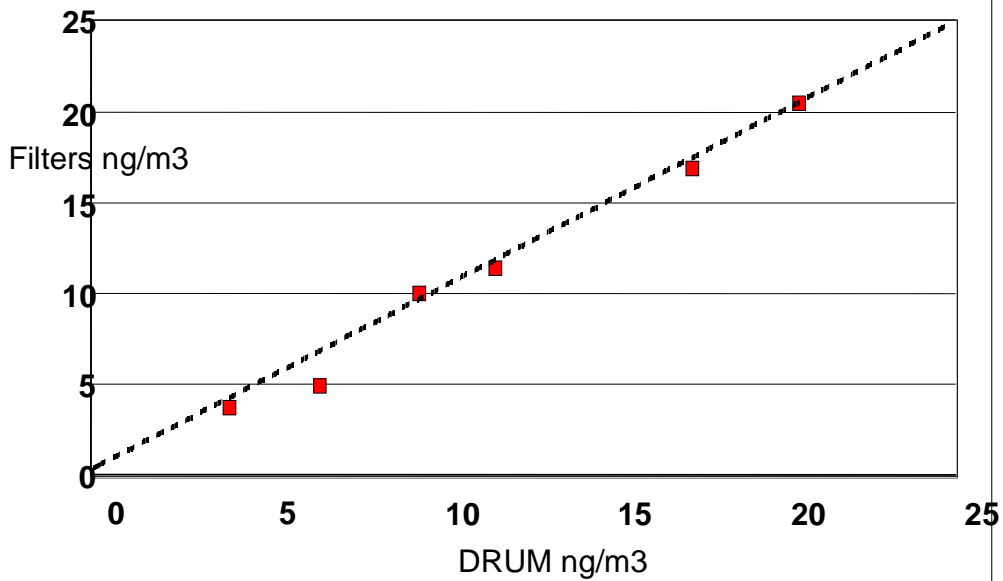
Iron



DELTA DRUM vs. ARB Filter Inter-comparison
Fresno March-April 2001
Copper



Zinc



Summary of filter inter-comparisons

QA addendum, DELTA Group Yosemite NP Study, Summer, 2002
 April 11, 2005

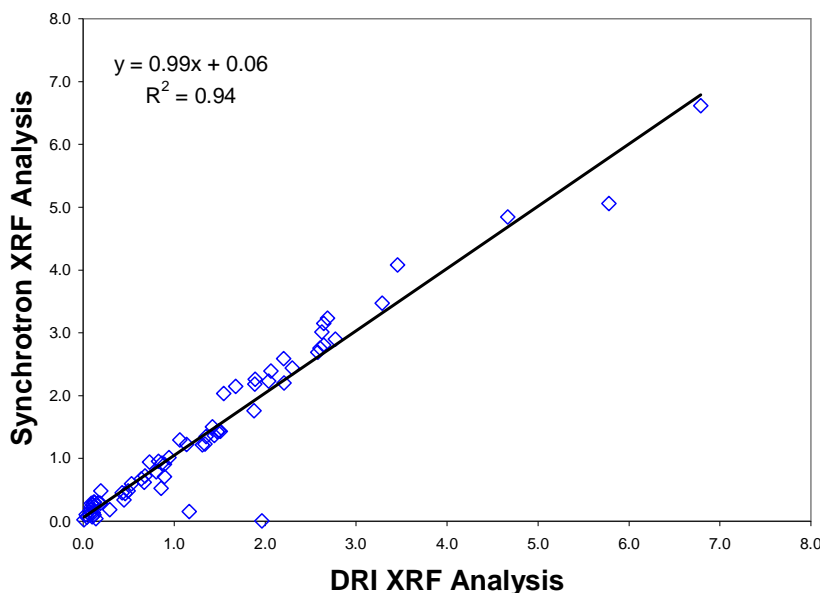
As a component of the Yosemite study, Teflon filters were collected every 24 hr using new IMPROVE modules located on Turtleback Dome circa 150 m south of the IMPROVE YOSE site. Filter operations were handled by IMPROVE and its collaborators in the study. The filters were analyzed for mass (IMPROVE CNL), elements by synchrotron x-ray fluorescence S-XRF (DELTA Group, UC Davis), and then XRF (IMPROVE CNL).

These results can be compared with the standard IMPROVE YOSE data used earlier in the Yosemite Final Report to isolate sampling versus analytical differences. In summary, agreement with sulfur was excellent (CNL/DELTA = 1.04 ± 0.07). Soils were highly correlated (r^2 circa 0.85) but with CNL seeing larger values than DELTA (1.40 ± 0.13 , with one anomalous Ti point removed; also note Sr = 1.45). The improvement in sensitivity in the Yosemite tests raised the yield of several elements, including aluminum, seen every day during the study but only 73% in the YOSE network data. The CNL filter data also confirmed the DELTA result showing a strange multi-day periodicity in the soils with a magnitude around 30%. The effect in potassium was much less than other soils, CNL/DELTA = 1.13 ± 0.09 , probably because potassium has a sub- $2.5 \mu\text{m}$ component from smoke and does not exhibit any string multi-day periodicity.

The rather weak agreement with IMPROVE was, we propose, a results of analytical deficiencies of the IMPROVE/CNL home built XRF system that by now are well known and routinely posted on the IMPROVE comments pages of the web site and at the AAAR meeting, October, 2003 (White et al, 2003).

XRF to S-XRF comparison for the California ARB, 2003 (below)

Silicon

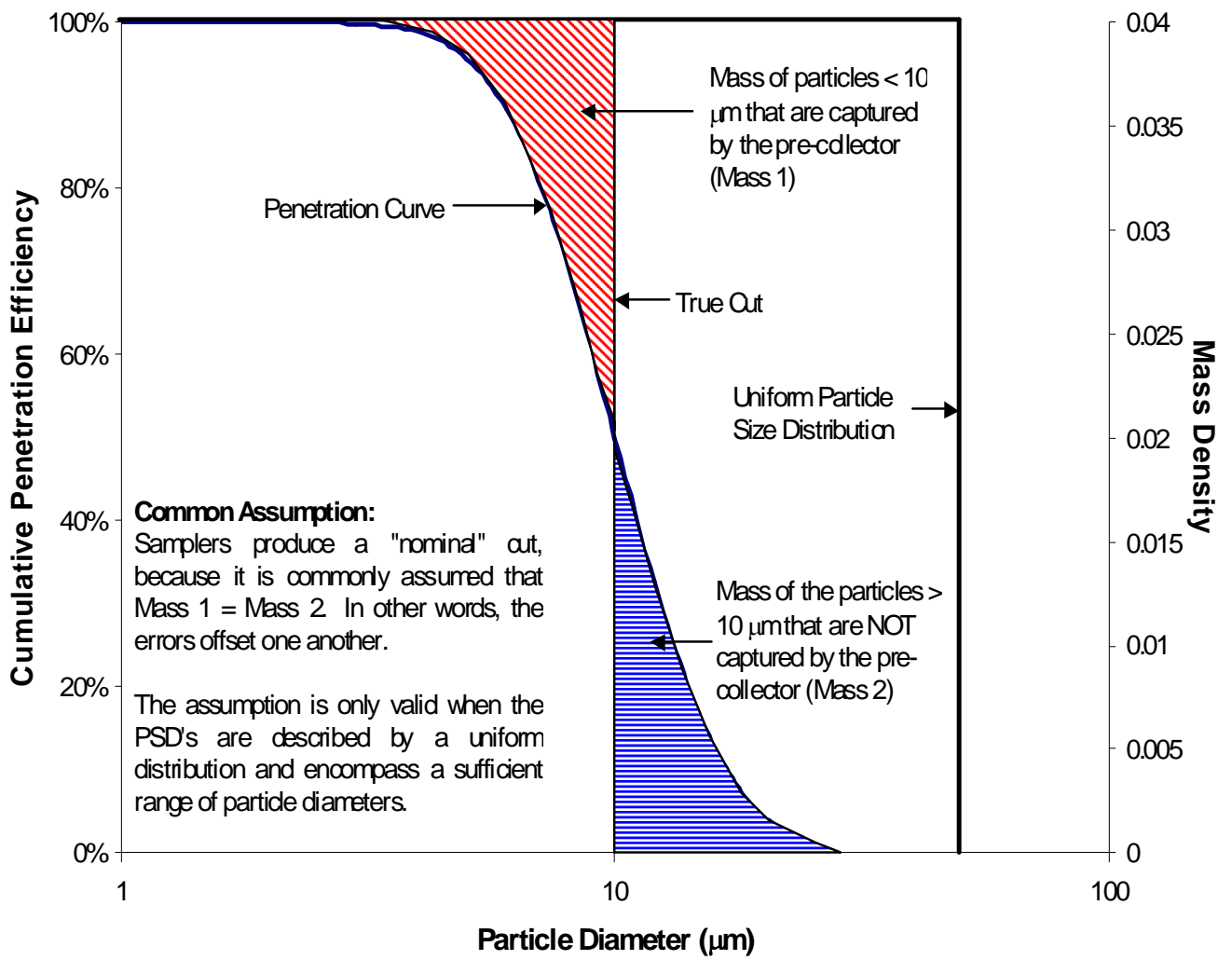


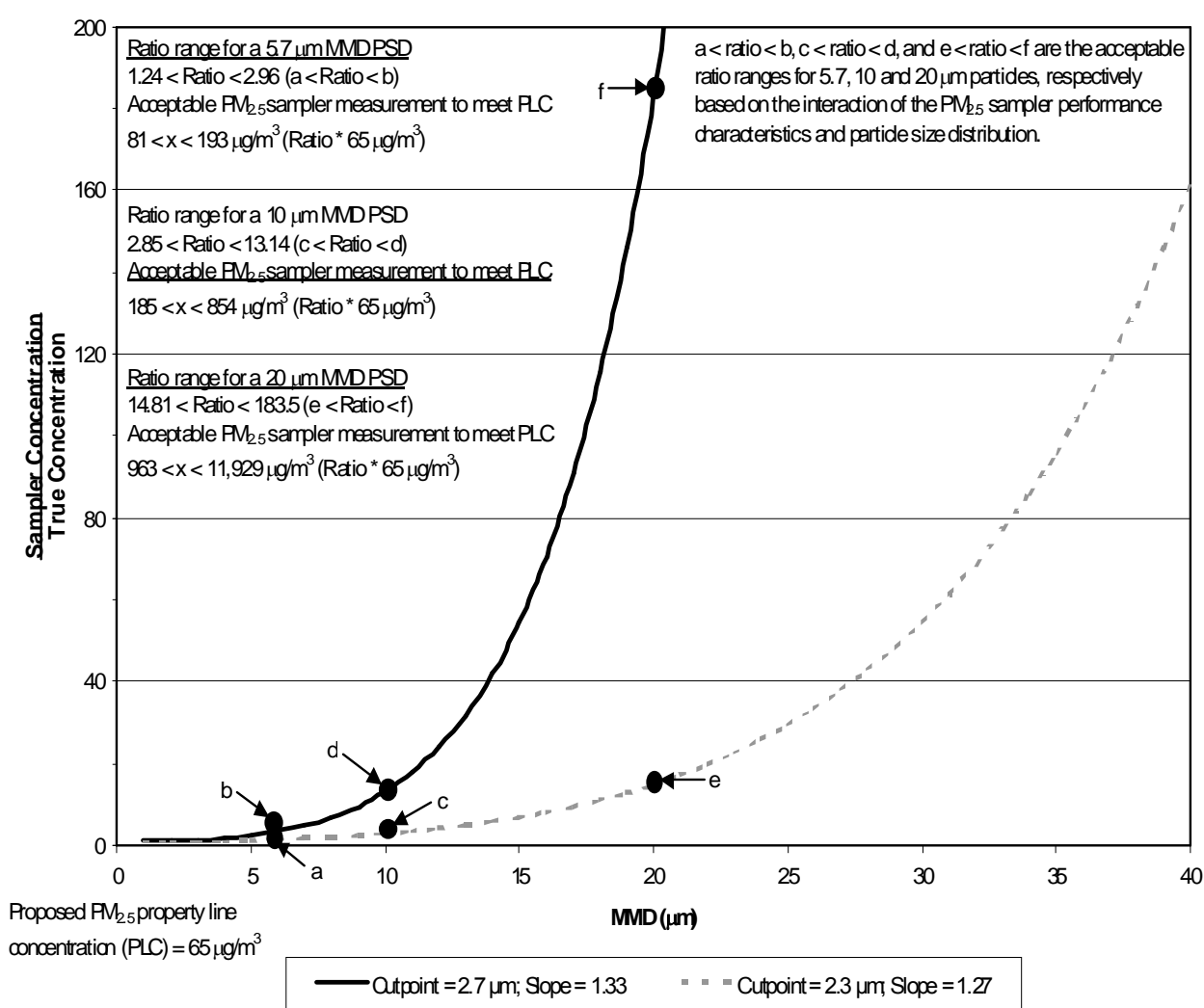
Far better agreement was obtained versus the Desert research Institute's 5 anode commercial XRF system in the Air Resources Board's Lake Tahoe Atmospheric Deposition (LTAD) study of 2003. Above we show the blind intercomparison of silicon between the two systems, which was similar for other major elements. For minor elements, including the important element phosphorus, the S-XRF was roughly 10 x more sensitive than DRI.

Below we summarize all DELTA Group S-XRF inter-comparisons in the past 5 years. Note that there were problems with the ARB RAAS analyses since the two internal ARB X-RF to ARB RAAS comparisons agreed only at the level 1.29 ± 0.63 for all co-measured elements. (DQAP v. 8.02, pg 32) We also give averages below without the ARB RAAS data.

Study and date	Methods	Average ratio, Al to Fe	Std. dev.	Average ratio, Cu to Pb	Std. dev.
BRAVO, 1999	PIXE vs S-XRF	0.99	0.04		
BRAVO, 1999	CNL XRF vs S-XRF			1.24	0.14
FACES, 2001	ARB XRF vs S-XRF	0.93	0.21	1.02	0.08
FACES, 2001	ARB RAAS vs S-XRF	(0.98)	0.27	(0.74)	0.23
ARB LTAD 2005	DRI XRF vs S-XRF	1.037	0.085	0.907	0.009
All prior studies	Average (no RAAS)	0.984 (0.985)	0.15 (0.11)	0.977 (1.055)	0.115 (0.076)
Yosemite 2004- 2005	CNL XRF vs S-XRF	1.34	0.19	1.46	0.33

From this table, it is clear that the disagreements with IMPROVE were then exception to years of excellent intercomparison.





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Appendix B - Particle Size Corrections for DRUM and MOUDI Samplers

The table below shows the multiplicative particle size matrix correction values calculated for particles with geometric diameters between 2.5 and 1.1 μm .

Element	Multiplicative Correction Factor	Element	Multiplicative Correction Factor	Element	Multiplicative Correction Factor
Na	1.272	Ti	1.019	As	1.010
Mg	1.259	V	1.013	Se	1.010
Al	1.193	Cr	1.014	Br	1.012
Si	1.106	Mn	1.013	Kr	1.000
P	1.079	Fe	1.013	Rb	1.000
S	1.043	Co	1.013	Sr	1.000
Cl	1.061	Ni	1.013	Y	1.000
Ar	1.043	Cu	1.010	Zr	1.000
K	1.025	Zn	1.009	Nb	1.000
Ca	1.023	Ga	1.010	Mo	1.000
Sc	1.021	Ge	1.010		

The second matrix correction is a layering correction. This correction is only necessary when more than one monolayer of material is deposited on the substrate thereby absorbing some of the fluorescence X-rays from the material located on the bottom. The development and testing of matrix correction algorithms will continue to be one of our major thrusts in the years to come. Additional details are available upon request.

Post AXIL Particle Size Corrections

		MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI	MOUDI
		stage	stage	stage	stage	stage	stage	stage	stage	stage	stage	stage	stage	stage	stage
Element	Energy	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	(keV)	18	10	5.6	3.2	1.8	1.0	0.56	0.32	0.18	0.10	0.056	0.032	0.018	0.01
Na	1.041	8.6	3.520	2.116	1.496	1.285	1.149	1.076	1.045	1.026	1.015	1.007	1.003	1.010	1.000
Mg	1.254	8.0	3.334	2.030	1.464	1.272	1.149	1.084	1.055	1.032	1.018	1.009	1.003	1.010	1.000
Al	1.487	6.2	2.732	1.745	1.341	1.203	1.112	1.063	1.041	1.023	1.012	1.006	1.003	1.010	1.000
Si	1.740	4.0	1.989	1.391	1.184	1.111	1.062	1.036	1.023	1.014	1.009	1.004	1.002	1.001	1.000
P	2.015	3.4	1.787	1.292	1.138	1.082	1.044	1.023	1.014	1.008	1.004	1.002	1.001	1.001	1.000
S	2.307	2.6	1.526	1.163	1.077	1.045	1.024	1.013	1.007	1.004	1.003	1.001	1.001	1.001	1.000
Cl	2.622	2.9	1.642	1.221	1.106	1.064	1.034	1.017	1.010	1.007	1.004	1.002	1.001	1.001	1.000
Ar	2.957	2.5	1.507	1.154	1.074	1.045	1.024	1.013	1.008	1.004	1.002	1.001	1.001	1.000	1.000
K	3.312	2.1	1.372	1.088	1.043	1.026	1.015	1.008	1.005	1.002	1.001	1.000	1.000	1.000	1.000
Ca	3.690	2.1	1.358	1.080	1.039	1.024	1.013	1.008	1.005	1.001	1.000	1.000	1.000	1.000	1.000
Sc	4.088	2.0	1.340	1.071	1.035	1.022	1.012	1.007	1.004	1.001	1.000	1.000	1.000	1.000	1.000
Ti	4.508	2.0	1.322	1.062	1.031	1.019	1.011	1.006	1.003	1.001	1.000	1.000	1.000	1.000	1.000
V	4.949	1.9	1.291	1.046	1.022	1.013	1.007	1.004	1.003	1.001	1.000	1.000	1.000	1.000	1.000
Cr	5.411	1.9	1.302	1.052	1.025	1.015	1.008	1.004	1.003	1.001	1.000	1.000	1.000	1.000	1.000
Mn	5.895	1.9	1.289	1.045	1.022	1.013	1.007	1.004	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Fe	6.400	1.9	1.286	1.044	1.021	1.013	1.007	1.005	1.003	1.001	1.000	1.000	1.000	1.000	1.000
Co	6.925	1.9	1.288	1.045	1.022	1.013	1.007	1.004	1.003	1.001	1.000	1.000	1.000	1.000	1.000
Ni	7.472	1.9	1.291	1.046	1.022	1.013	1.007	1.004	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Cu	8.041	1.8	1.274	1.038	1.018	1.011	1.006	1.003	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Zn	8.631	1.8	1.265	1.033	1.016	1.009	1.005	1.003	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Ga	9.243	1.8	1.274	1.038	1.018	1.011	1.006	1.003	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Ge	9.876	1.8	1.274	1.038	1.018	1.011	1.006	1.003	1.002	1.001	1.001	1.000	1.000	1.000	1.000
As	10.532	1.8	1.274	1.038	1.018	1.011	1.006	1.003	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Se	11.210	1.8	1.274	1.038	1.018	1.011	1.006	1.003	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Br	11.907	1.9	1.284	1.042	1.020	1.012	1.006	1.003	1.002	1.001	1.001	1.000	1.000	1.000	1.000
Pb	10.543	1.9	1.313	1.058	1.028	1.016	1.009	1.005	1.003	1.002	1.002	1.000	1.000	1.000	1.000

Note: The value for MOUDI Stage 1 is merely an estimate, +/- 30%.

Appendix E - Comparison of Analyses, IMPROVE vs. DELTA, BRAVO

Comparison between analyses - BRAVO filters

April, 2002

CNL IMPROVE PIXE + XRF versus DELTA Group S-XRF

All values in ng/cm²

Average, 6 major PIXE elements			0.95
	Al,Si,S,K,Ca,Fe	std dev	0.08
Average, 5 major XRF elements			1.13
	Cu,Zn,Br,Sr,Pb	std dev	0.95
Average, all elements, non zero ratios			1.33
		std dev	3.40
			0.48
		BR2 B BR2	0.74

C N PI	CNL XRF	DELTA S-XRF Element	CNL PIXE Oct 4	CNL XRF	DELTA average	DELTA std	BR2 A4 08:00 AM 16 blank to deposit DELTA	B BR2 3 edge of filter blank blank _{0,1, 20}	Ratio
									CNL/ DELT
p		Na	2503.96		978.9	208.8		0.0	2.6
p		Mg	0		300.1	141.4		0.0	0.0
p		Al	1674.67		2049.6	249.9		16.5	0.8
p		Si	4473.93		4719.8	500.5		56.4	0.9
p		P	0		812.1	79.6		5.4	0.0
p	s	S	14510.67	16303.4	15971.0	1574		259.6	0.9
p	cl	Cl	0	0	54.8	12.8		0.4	0.0
p	k	K	711.01	0	740.0	85.0		7.5	1.0
p	ca	Ca	2360.02	2426.76	2417.2	240.5		28.4	1.0
pt	ti	Ti	145.8	104.28	169.7	28.9		21.1	0.9
p	v	V	10.31	0	17.7	7.3		0.9	0.6
p	cr	Cr	47.23	0	2.5	1.0		0.4	19.1
p	mn	Mn	29.76	0	24.0	10.1		0.5	1.2
pf	fe	Fe	1096.07	1040.26	994.7	131.5		12.3	1.1
p	co	Co	0	0	6.48	1.2		0.74	0.0
p	ni	Ni	0	0	49.99	9.8		2.64	0.0
p	cu	Cu	33.23	0	12.00	2.4		3.08	0.0
p	zn	Zn	68.61	25.08	29.75	5.2		4.25	0.8
p	ga	Ga	0	0	0.16	0.3		0.39	0.0
p	as	As	0	4.43	1.99	3.6		0.00	2.2
p	se	Se	0	4.47	2.14	1.6		0.00	2.1
p	br	Br	0	31.95	12.65	3.4		0.54	2.5
	rb	Rb		0	1.27	2.2		1.44	0.0
	sr	Sr		9.99	5.27	5.4		0.00	1.9
	y	Y		0	2.01	2.7		0.00	0.0
	zr	Zr		0	2.87	3.3		0.00	0.0
		Mo			9.20	8.5		5.19	0.0

Average MDLs				BRAVO BR2 October 4			BRAVO BR4 October 22		
CNL PIXE+ XRF Element nt (Switches at Fe)	CNL MDL PIXE + XRF	DELTA S-XRF Element	DELTA MDL S-XRF	CNL PIXE + XRF	DELTA average 16 points	DELTA error	CNL PIXE + XRF	DELTA average 10 points	DELTA std
pna	147.6	Na	8.8	2504	979	208.8	0	18	20
pmg	84.9	Mg	7.0	0	300	141.4	0	111	35
pal	47.8	Al	3.1	1675	2050	249.9	442	580	57
psi	37.6	Si	1.6	4474	4720	500.5	1336	1329	106
pp	34.1	P	1.0	0	812	79.6	0	277	15
ps	33.4	S	1.3	14511	15971	1574	3955	4316	294
pcl	32.4	Cl	0.4	0	55	12.8	0	18	2
pk	22.4	K	0.3	711	740	85.0	268	291	20
pca	17.5	Ca	0.3	2360	2417	240.5	872	821	103
pti	17.1	Ti	0.9	146	170	28.9	34.7	45.1	7.5
pv	0.3	V	0.2	10	18	7.3	0.5	2.2	2.9
pcr	11.3	Cr	0.1	47	2	1.0	12.5	0.6	0.6
pmn	11.5	Mn	0.1	30	24	10.1	17.9	8.2	4.4
fe	2.0	Fe	0.2	1040.3	994.7	131.5	387.6	472.4	531.5
co	na	Co	0.2	0	6.5	1.2	0	4.2	3.1
ni	1.6	Ni	0.2	0	50.0	9.8	0	4.1	1.6
cu	1.2	Cu	0.3	0	12.0	2.4	0	2.8	0.8
zn	0.8	Zn	0.2	25.1	29.8	5.2	8.9	9.9	2.1
ga	0.6	Ga	0.2	0	0.2	0.3	0	0.3	0.2
as	0.5	As	0.4	4.4	2.0	3.6	0	1.1	1.1
se	0.6	Se	0.3	4.5	2.1	1.6	0	1.2	0.7
br	0.6	Br	0.4	32.0	12.6	3.4	16.9	7.7	0.9
rb	1.0	Rb	0.6	0	1.3	2.2	0	1.3	1.3
sr	1.0	Sr	0.7	10.0	5.3	5.4	2.3	0.9	0.9
y	1.2	Y	0.9	0	2.0	2.7	0	0.5	0.8
zr	1.6	Zr	1.2	0	2.9	3.3	0	1.5	2.5
		Mo	1.5		9.2	8.5	0	4.8	7.5
pb	1.1	Pb	1.7	4.2	11.7	15.9	0	3.9	4.8

CNL PIXE + XRF	BRAVO BR5 October 29		CNL PIXE + XRF	BRAVO BR6 October 30		CNL PIXE+ XRF	Average MDLs		DELTA S-XRF	DELTA MDL S- XRF
	DELTA average	DELTA std		DELTA average	DELTA std		CNL MDL PIXE + XRF	Element		
	14 points			14 points		Element (Switches at Fe)		Element		
1106	203	95	101	48	38	pna	147.6	Na	8.8	
0	769	136	0	124	27	pmg	84.9	Mg	7.0	
3432	3672	213	444	479	36	pal	47.8	Al	3.1	
9229	7723	443	1095	1095	86	psi	37.6	Si	1.6	
0	649	44	0	111	9	pp	34.1	P	1.0	
11507	11258	375	1691	1878	104	ps	33.4	S	1.3	
0	44	7	0	10	2	pcl	32.4	Cl	0.4	
1834	1733	79	232	224	13	pk	22.4	K	0.3	
3943	3525	250	456	410	40	pca	17.5	Ca	0.3	
178	197	13.2	52	36.0	4.9	pti	17.1	Ti	0.9	
43	54	6.5	0	1.9	0.3	pv	0.3	V	0.2	
0	1.6	1.4	19	0.1	0.1	pcr	11.3	Cr	0.1	
82	60	7.7	0	4.6	0.7	pmn	11.5	Mn	0.1	
2084.6	1825.7	107.7	231.1	194.7	21.0	fe	2.0	Fe	0.2	
0	13.4	1.9	0	2.1	0.3	co	na	Co	0.2	
0	10.5	1.9	0	1.3	0.4	ni	1.6	Ni	0.2	
0	9.5	1.8	0	1.5	0.3	cu	1.2	Cu	0.3	
123.0	115.9	9.4	4.4	4.7	0.7	zn	0.8	Zn	0.2	
0	0.5	0.6	0	0.3	0.3	ga	0.6	Ga	0.2	
0	4.2	5.5	0	1.2	1.4	as	0.5	As	0.4	
1.2	1.1	1.6	1.0	0.8	0.4	se	0.6	Se	0.3	
35.1	15.0	1.6	9.6	4.5	1.0	br	0.6	Br	0.4	
7.4	7.2	4.6	0	0.5	0.7	rb	1.0	Rb	0.6	
18.1	8.2	6.8	1.8	0.7	1.0	sr	1.0	Sr	0.7	
0	3.1	3.7	0	1.4	1.5	y	1.2	Y	0.9	
0	6.0	5.3	0	2.3	1.9	zr	1.6	Zr	1.2	
0	12.4	10.6	0	4.9	6.1			Mo	1.5	
33.9	19.6	22.0	0	4.7	6.2	pb	1.1	Pb	1.7	

Appendix F - Comparison of Standard Samples Using EPA Method 3052 and ICP/MS

In the course of the NSF-funded ACE-Asia study, problems were discovered in analyses of standard samples CJ-1 Chinese loess sample with the standard digestion technique EPA Method 3052. This information is included herein as it bears upon attempts to compare data from the DRUM plus S-XRF analysis to filters analyzed by ICP/MS. This is not a new problem, as it had earlier occurred in the Air and Industrial Hygiene Laboratory's Atomic Absorption Spectroscopy analyses, giving highly precise and repeatable results that were sharply in error (by as much as 47 standard errors!). This was found during an EPA/DOE side by side comparison in Charleston, West Virginia, reported in 1978 (Cahill, 1980). The problem with any fluid-based analytical system is getting the materials from the solid phase on the filters into the fluid medium in the instrument. A variety of techniques using heat, microwaves, and strong acids have to be employed, and these are not equally effective for all chemical compounds. In the ACE-Asia study, the EPA method 3052 gave yields between 34.5% to 99.2% depending on the element (one value of 305% for copper is probably a contaminated solute, since the boric acid value agrees with the standard. It does highlight the extreme sensitivity of ICP/MS to clean solutes and good laboratory practices). The problem was solved in the laboratory by using additional steps including a boric acid digestion.

Techniques:

Analysis of CJ-1 Reference Sample

The loess reference sample CJ-1 was prepared by three methods as follows:

1. (EPA) Method 3052 digestion: to a 0.1 g sample add 5 mL H₂O 7 mL HNO₃, 3 mL HCl, 5 mL HF, and 1 mL H₂O Seal and heat in microwave for 30 minutes. Cool in hood and dilute to 50 mL.
2. Boric acid digestion: to a 0.1 g sample add 5 mL HNO₃ and 3 mL HF. Heat in microwave for 15 minutes, cool in freezer, open and add 25 mL of 6% boric acid solution. Seal and heat in microwave for 5 minutes. Cool in hood. Open and dilute to 50 mL. One of these preparations was spilled and those data are not reported.
3. A modified boric acid preparation: to 0.1 g sample add 5 mL H₂O 1 mL HF and 5 mL 6% boric acid, then dilute to 20 mL. Seal, heat, cool and dilute as above. The sample digests were prepared analyzed in duplicate with good precision between duplicates.

All analyses were performed using a Perkin-Elmer Elan 6000 ICP-MS.

Appendix G - XRF NIST Traceable Calibration Standard Certification for S-XRF

- 59 standards, 65 certified values
Micromatter Co. NIST traceable standards Li -U
jheagney@micromatter.com
- NIST SRM # 1832, and 1833, 12 certified elements, Al – Pb

Standard Compound	Serial #	Aereal density $\mu\text{g}/\text{cm}^2 \pm 5\%$	Element 1 $\mu\text{g}/\text{cm}^2 \pm 5\%$	Element 2 $\mu\text{g}/\text{cm}^2 \pm 5\%$
Lithium as LiF	12518	45.6		
Sodium Chloride	12519	46.0	18.1	27.9
Magnesium metal	12520	48.7		
Aluminum metal	12521	51.0		
Silicon as SiO	12522	45.1	28.7	
Phosphorus or gallium as GaP (not stoichiometric)	12523	43.7		
Sulfur, copper as CuS_x	12524	66.0	47.9	18.1
Chlorine or Potassium as KCl	12525	46.1	24.2	21.9
Potassium or Iodine as KI	12526	51.5	12.1	Not given
Calcium as CaF_2	12527	47.5	24.4	39.4
Scandium as ScF_3	12528	49.5		
Titanium as Ti metal	12529	44.5		
Vanadium as V metal	12530	47.5		
Chromium as Cr metal	12531	47.5		
Manganese as Mn metal	12532	42.8		
Iron as Fe metal	12533	48.2		
Cobalt as Co metal	12534	49.2		
Nickel as Ni metal	12535	50.7		
Copper as Cu metal	12536	44.5		
Zinc as ZnTe (not stoichiometric)	12537	53.4		
Germanium as Ge metal	12538	46.0		
Arsenic as GaAs (not	12539	51.8		

stoichiometric)				
Selenium as Se metal	12540	48.8		
Bromine or Cesium as CsBr	12541	50.4	31.5	18.9
Rubidium of Iodine as RbI	12542	52.0	20.9	31.1
Strontium as SrF ₂	12543	47.6	33.2	
Yttrium as YF ₃	12544	51.4	31.3	
Niobium as Nb ₂ O ₃	12545	52.9	42.0	
Molybdenum as MoO ₃	12546	52.2	34.8	
Rhodium as Rh metal	12547	44.3		
Palladium as Pd metal	12548	43.1		
Silver as Ag metal	12549	43.7		
Cadmium as CdSe (not stoichiometric)	12550	46.8		
Indium as In metal	12551	48.0		
Tin as Sn metal	12552	45.2		
Antimony as Sb metal	12553	50.8		
Tellurium as Te metal	12554	43.1		
Barium as BaF ₂	12555	46.7		
Lanthanum as LaF ₃	12556	44.1		
Cerium as CeF ₃	12557	46.5		
Praseodymium as PrF ₃	12558	47.2		
Neodymium as NdF ₃	12559	51.2		
Samarium as SmF ₃	12560	51.2		
Europium as EuF ₃	12561	40.9		
Gadolinium as GdF ₃	12562	50.2		
Terbium as TbF ₃	12563	47.2		
Dysprosium as DyF ₃	12564	48.8		
Holmium as HoF ₃	12565	50.2		
Erbium as ErF ₃	12566	47.3		
Thulium as TmF ₃	12567	46.0		
Ytterbium as YbF ₃	12568	50.0		
Lutetium as LuF ₃	12569	46.0		

Tungsten as WO ₃	12570	49.3		
Platinum as Pt metal	12571	45.1		
Gold as Au metal	12572	44.8		
Thallium as TlCl	12573	43.6		
Lead as Pb metal	12574	52.4		
Bismuth as Bi metal	12575	45.7		
Thorium as ThF ₄ (radioactive) ?!	12576	51.6		
Uranium as UF ₄	12577	46.3		
Backing 6.3 micron Mylar, deposit to rings				
NIST 1832	Al 12.1	Si 28.7	Ca 18.1	V 4.5
	Mn 4.3	Co 0.98	Cu 2.3	
(note: requires abs corr.)				
NIST 1833	Si 29.1	K 16.5	Ti 12.6	Fe 14.2
	Zn 3.9			
(note: requires abs corr.)				
