Analysis of air filters using the ARL QUANT'X EDXRF Spectrometer

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INTRODUCTION

The United States Environmental Protection Agency's (U.S. EPA) commitment to improve air quality across the USA has created an increasing demand for the monitoring of specific elements in ambient particulate matter collected on filters in residential, industrial and recreational areas. X-ray fluorescence is the preferred method to analyze samples related to air monitoring due to the non-destructive nature of the technique and the superior sensitivity achievable.

The Thermo Scientific™ ARL™ QUANT'X Energy Dispersive X-Ray Fluorescence (EDXRF) instrumentation is ideal for determining concentrations of multiple elements on air filters. The bench top instrument is capable of analyzing the elements sodium to americium with minimal sample preparation and can accommodate filter sizes from 25 mm to 47 mm in diameter using a sample changer or up to 220 mm if loaded manually.

The ARL QUANT'X Spectrometer is equipped with a state-of-the-art silicon drift detector (SDD) with excellent resolution minimizing spectral interference while providing excellent response. Its large active area of 30 mm^2 ensures a large solid angle for efficient X-ray collection. A high-flux rhodium anode tube, positioned to allow direct excitation from the X-ray tube or tailored excitation through a choice of nine different filters, maximizes sensitivity for a wide range of elements.

INSTRUMENT

The key benefits that make the ARL QUANT'X Spectrometer one of the leading instruments in the field of air filter monitoring are listed below:

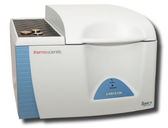
- Silicon Drift Detector (SDD) with a typical resolution of 135 eV at Mn Kα
- Excellent overall sensitivity thanks to large area detector crystal
- High-flux 50 W rhodium anode X-ray tube with excitation voltage of 4 to 50 kV adjustable by steps of 1 kV
- 9-position X-ray tube filter wheel to maximize sensitivity for a wide range of elements
- 10-position automated sample changer (20-position version for 32 mm diameter samples)
- Elemental range covering sodium (Z=11) to americium (Z=95)
- Multiple element analysis under a single analytical condition
- Wide dynamic range: ppm to percent
- Capable of analyzing various sample types and sizes
- Fast digital pulse processing for increased throughput
- Choice of 5 primary tube collimators (1.0 mm to 8.8 mm)
- Ethernet connectivity for remote access
- Thermo Scientific™ UniQuant™ Software for Standardless XRF Analysis enabling elemental analysis of samples with or without the use of standards
- Thermo Scientific™ WinTrace Software with integrated empirical, fundamental parameters and thin film modules

In addition to the above benefits, the technical features below support an instrument which provides years of reliable service:

- Field transportable and rugged for mobile use
- Low maintenance cost
- Mechanically simple
- Long term stability – individual calibrations remain within QC specifications for months

EXCITATION CONDITIONS

The ARL QUANT'X Spectrometer employs filtered radiation to optimally excite the sample and cause its constituent elements to fluoresce. The ARL QUANT'X Spectrometer is equipped with a nine-position filter wheel to reduce spectrum background and tailor excitation energy. The various acquisition parameters are selected for optimal excitation of the elements of concern and best limits of detection.



SAMPLE PREPARATION AND PRESENTATION

Air filters require no sample preparation prior to analysis except for an inspection of the filter to identify any defects that may affect the analytical results. The filters are analyzed under vacuum conditions to eliminate the ambient atmosphere between the sample and detector which would otherwise absorb the characteristic X-rays of light elements. The use of vacuum significantly improves light element sensitivity.

The filters are loaded into a 10-position auto-sampler tray if greater than 31 mm in diameter and a 20-position auto- sampler tray if the sample diameter equals 31 mm or less. The auto-sampler trays feature removable sample holders and inserts to accommodate various size filters.

QUANTITATIVE ANALYSIS

Analysis of air filters is accomplished following the U.S. EPA Compendium Method IO-3.3 titled Determination of Metals in Ambient Particulate Matter as modified for use with the ARL QUANT'X Spectrometer.

Empirical calibrations are achieved using commercial, single and dual element, thin film standards from MicroMatter Technologies Inc. in addition to blank films. Verification of the element calibrations is accomplished by analyzing a National Institute of Standards and Technology (NIST) standard reference material (SRM) 2783 *Air particulate on filter media*.

Figure 1 shows a spectrum acquired with the ARL QUANT'X Spectrometer on NIST SRM 2783 *Air particulate on filter media* with elements of interest identified. In this case an excitation voltage of 50 kV, thick Pd filter and a measurement time of 300 s was used. The excellent spectral resolution and associated peak-to-background ratios allows for element lines that are well separated.

Figure 1. Spectrum of NIST SRM 2783 Air particulate on filter media

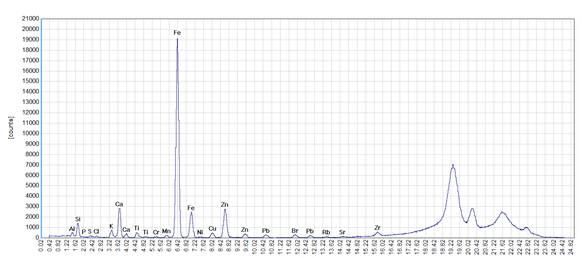


Table 1 below shows the five excitation conditions which are used for the analysis. These are optimized for different groups of elements. The total measurement time per sample is 25 minutes. Measurement time per condition can be tailored according to specific application requirements.

The WinTrace Software uses an advanced deconvolution algorithm to calculate net peak intensities that are corrected for any overlap by neighboring peaks. This allows for a much more accurate analysis compared to a simple region of interest (ROI) approach around element peaks of interest.

Table 1. Excitation conditions.

Condition	Filter	Voltage (kV)	Atmosphere	Live Time (s)	Elements
Low Za	None	4	Vacuum	300	Na, Mg
Low Zb	Thick C	15	Vacuum	300	Al, Si, P, S, Cl, K, Ca, Sc, Ag, Cd, Sn, Sb, Te, I
Low Zc	Al	20	Vacuum	300	Ti, V, Cr, Mn, Cs, Ba, La
Mid Zc	Thick Pd	50	Vacuum	300	Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Hg, Tl, Pb, Bi
High Za	Thin Cu	50	Vacuum	300	Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I

LIMITS OF DETECTION

Minimum detection limits (MDLs) are an important analytical component as they define the limitations and analytical quality of the acquired data. The determination of MDLs for ambient air filter analysis is achieved through the repeated analysis of multiple laboratory blanks. The ARL QUANT'X Spectrometer MDLs displayed in Table 2 are calculated using the average instrument uncertainty obtained on ten laboratory blanks. The ARL QUANT'X Spectrometer data is compared to those specified in the U.S. EPA Compendium Method IO-3.3. The MDLs are reported as 1σ (68% confidence level) as outlined in the U.S. EPA Compendium Method.

For a majority of elements listed, the MDLs achievable with the ARL QUANT'X Spectrometer are as good as or better than those stated by the U.S. EPA in Compendium Method IO-3.3. The detection levels calculated for the ARL QUANT'X Spectrometer range from less than 1 ng/cm^2 to 21 ng/cm^2. For a number of elements listed in Table 2 an extra value is given between parentheses. This is the MDL 1σ value calculated for the L lines of these elements. Though L lines of these elements typically suffer more from spectral interference than the corresponding K lines, a better MDL is sometimes attainable.

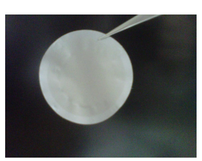


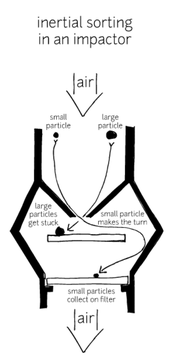
Table 2. Comparison of ARL QUANT'X Spectrometer limits of detection and U.S. EPA method.

Analyte	ARL QUANT'X MDLs 1σ, ng/cm^2	Method IO-3.3 MDLs 1σ, ng/cm^2	Analyte	ARL QUANT'X MDLs 1σ, ng/cm^2	Method IO-3.3 MDLs 1σ, ng/cm^2
Na	4.6	5.3	As	0.2	0.8
Mg	1.7	3.2	Se	0.1	0.7
Al	1.9	17.6	Br	0.6	0.6
Si	0.9	8.0	Rb	0.3	0.7
P	0.9	2.6	Sr	0.4	1.1
S	0.9	2.6	Y	0.3	1.2
Cl	0.6	4.8	Zr	0.8	1.2
K	0.3	6.3	Mo	0.2	1.6
Ca	0.2	9.0	Pd	3.0	22.9
Sc	0.4	1.5	Ag	3.0	20.2
Ti	0.2	16.9	Cd	4 (0.6)	22.0
V	0.2	5.3	Sn	16 (1.0)	30.5
Cr	0.2	3.0	Sb	21 (1.3)	31.4
Mn	0.2	0.8	Cs	0.7	48.9
Fe	0.3	0.7	Ba	0.6	51.8
Co	0.1	0.4	La	0.1	70.6
Ni	0.2	0.6	W	1.0	3.4
Cu	0.5	0.7	Au	0.5	1.7
Zn	0.4	1.0	Hg	0.5	1.5
Ga	0.3	1.6	Pb	0.4	1.5

( ) MDL obtained using L lines

CONCLUSION

These results show the state-of-the-art performance achieved by an ARL QUANT'X Spectrometer regarding the analysis of air particulate matter collected on filter media. The detection levels range from less than 1 ng/cm^2 to a few ng/cm^2. Performance for heavy and light elements alike is extremely good. All ARL QUANT'X Spectrometer detection limits are well below those expected in the EPA's Compendium Method IO-3.3.



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