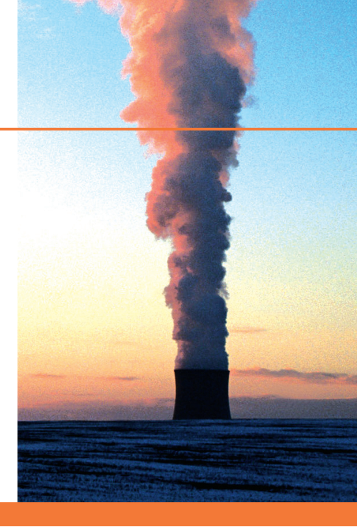

Analysis of Suspended Particulates Offers Key to Air Quality in Asia

AIR Monitoring

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The chemical analysis of suspended particulate matter in air is traditionally performed by energy dispersive X-ray fluorescence technology (EDXRF) according to EPA method IO-3.3, a protocol for the analysis of 44 elements on Teflon air filters. This article discusses the growing concerns about air quality in Asia, notes the significant advances in the development of EDXRF instrumentation and software that have occurred since the publication of the IO-3.3 method and presents an application study to demonstrate that by using the PANalytical Epsilon 5 EDXRF analyser the elemental range can be extended from 44 to 55 elements, using the EPA method.

Introduction

The toxicity of air pollutants is causing increasing concern throughout the world. One of the key areas of current research is into the suspended particulate matter content (SPM) of air. Historically, the measurement of SPM focussed on total suspended particulates, with no preference to size selection. More recent studies into the health effects of SPM have shifted the focus onto smaller particles that can be inhaled into the respiratory system. Small particles with toxic materials adsorbed onto the surface are especially damaging for human health. Ultrafine particles have also been found to have adverse health effects even when they are not associated with toxic materials, or where they are made up of substances that are not harmful when present as larger particles.

Air Pollution in Asia

SPM is a major concern in Asia where growing urbanisation is intensifying the problems caused by all air pollutants. Asia has already experienced extensive urbanisation and a further dramatic increase is projected – the urban population of Asia is expected to triple from 360 million in 1990 to over a billion by 2020 (UNDP, 1999). The World Health Organisation (WHO) reports that of the 15 cities with the highest levels of particulate matter in the world, 12 are in Asia.

The known health consequences of air pollution are considerable. SPM concentrations exceeding WHO standards can cause premature mortality and respiratory disease. The urban populations of China and Mongolia experience some of the world's highest exposure rates to harmful airborne particles, and even in Asian countries where the situation is improving, such as South Korea, standards still fall below WHO guidelines.

Monitoring SPM

Studying levels of SPM in ambient air is therefore essential to address the long-term health problems it can cause. In the United States, air quality standards are governed by the Clean Air Act and administered by the US Environmental Protection Agency (EPA). To analyse elemental composition of SPM, the EPA employs high volume air samplers that pre-concentrate SPM onto Teflon filters. The chemical analysis of SPM on these filters is traditionally performed by energy dispersive X-ray fluorescence technology (EDXRF) according to EPA method IO-3.3, a method that outlines a protocol

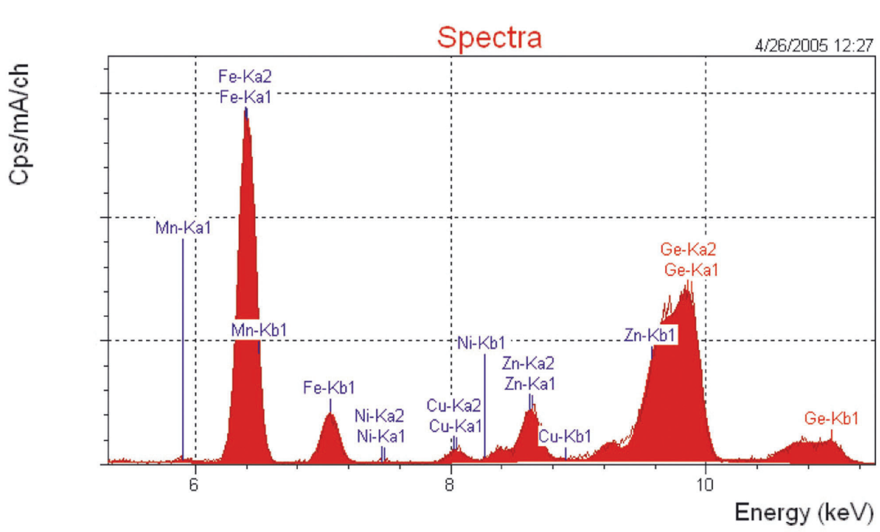

Figure 1: Spectrum of standard NIST 2783, obtained using the Ge secondary target.

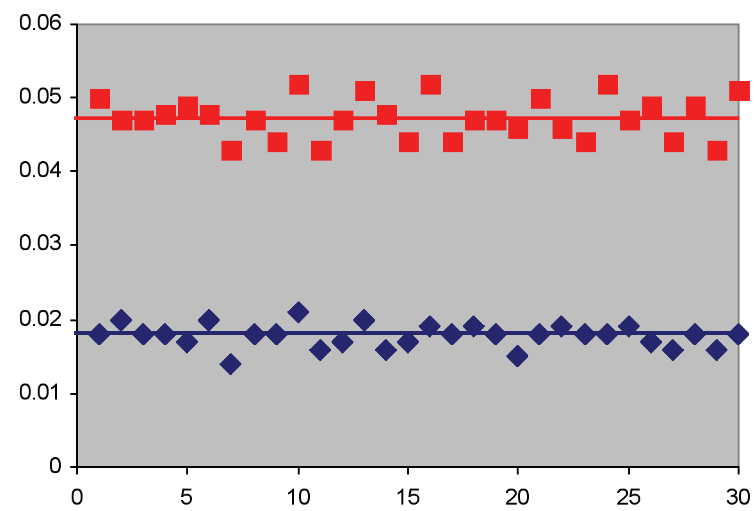

Figure 2: Short and long-term stability measurements of Cr and Cu in sample NIST 2783

for the analysis of 44 elements on Teflon air filters. However, significant advances in the development of EDXRF instrumentation and software have occurred since the publication of the IO-3.3 method. This article presents an application study to demonstrate that by using the PANalytical Epsilon 5 EDXRF analyser the elemental range can be extended from 44 to 55 elements, using the EPA method IO-3.3:

Measurement Criteria and Calibration

The air filters application used in this study was set up according to EPA method IO-3.3 - an EDXRF method for the chemical analysis of airborne particulate matter in the 2.5 - 10 µm size range ($PM_{2.5}$ and PM_{10}). The method specifies the analysis of 44 elements in the ng/cm² range.

For this study the analytical measurement parameters were optimised to accommodate the technological improvements incorporated into the PANalytical Epsilon 5 - a fully integrated EDXRF analysis system that utilises 3-dimensional, polarising optical geometry. The method was set up and calibrated with 59 commercially available air filter standards and a blank sample from Micromatter Co. (Eastsound, WA). The standards were composed of pure elements and compounds deposited on 40mm Nucleopore media.

The calibration was established using a single standard and a blank for each element. A Fundamental Parameter (FP) method was used to allow for the difference in sample loading when analysing unknowns. The measurement parameters used for this application are shown in table 1. The measurement time per condition was 100 seconds, except for the CaF_2 target which was 600 seconds.

Performance

The Epsilon 5 software features a very powerful deconvolution algorithm that analyses the sample spectrum and determines the net intensities of element peaks, even when they overlap one another. The accuracy with which this is carried out is essential to trace element analysis.

Figure 1 shows a fitted spectrum of air filter standard NIST 2783 obtained with the Ge secondary target. The extremely low background is a consequence of the polarising optical path.

Precision and Accuracy

The total method precision is a combination of instrument precision and stability of the sample during measurement. The method precision can be reported for both short (repeatability) and long term

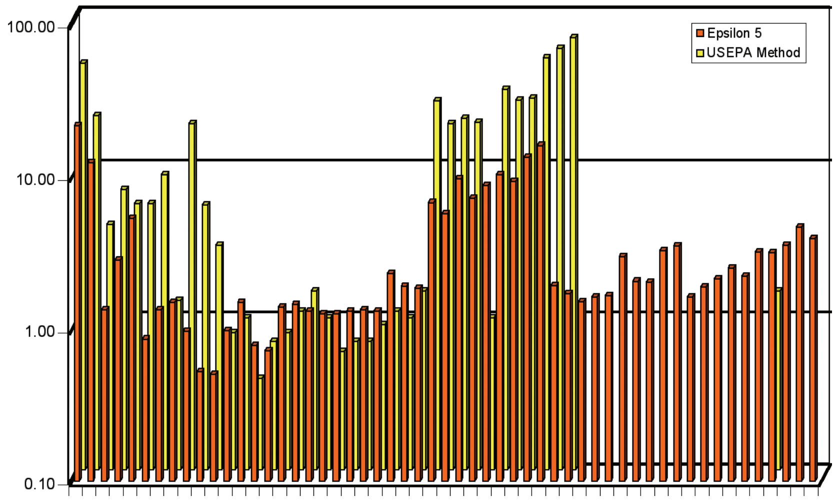

Figure 3: Detection limits (1 sigma) for air filters using the Epsilon 5 compared with those reported by the EPA (reports only elements up to La, except for Pb)

(reproducibility) measurements. Epsilon 5's repeatability was assessed by taking 20 measurements in one day of a single filter sample (NIST 2783). Reproducibility was determined by measuring the same sample once per day over a 10-day period.

The repeatability and reproducibility data for a selection of elements are shown in table 2. No drift correction was applied during the precision studies. The repeatability and reproducibility are both excellent and for most elements the short and long term precision are nearly identical. Comparison of the relative RMS values with the counting statistical error (theoretically, the minimum possible error) shows the excellent precision of the instrument and the non-destructive nature of the method for analysing filter samples. Figure 2 gives a graphical representation of the short and long-term stability of Cr and Cu.

The accuracy of the method was determined by comparing results of the NIST 2783 standard. The results of the selected elements are shown in table 3 and show a good agreement with the certified values.

Detection Limits

Detection limits are an important measure of an instrument's performance. The detection limits for this application were calculated from 50 replicate measurements of a Teflon blank sample and are based on 1 sigma (as specified in method IO-3.3). Calculations are based on a measurement time of 400 seconds per condition, which is chosen to give a better comparison with the values as reported by EPA. The detection limits for 55 elements are shown in figure 3 and compared with the detection limits as reported by the EPA.

The detection limits obtained with the Epsilon 5 range from 20 ng/cm² to less than 1 ng/cm². Across the majority of the elemental range the detection limits are better or comparable with those quoted by the EPA. The high sensitivity of the Epsilon 5 for measuring elements across the periodic table is a direct result of the combination of the 100 kV dual-anode x-ray tube, a wide range of secondary targets and lowered background due to the polarizing geometry of the optical path.

Conclusions

Air quality monitoring and data collection are vital components of any strategy that aims to reduce air pollution and its harmful effects on human health. As well as informing policy decisions, data can be used to advise people of current pollution risks and to ensure compliance with air quality standards. Measuring air pollutants may also lead to the identification of pollution sources.

The evidence correlating air pollution and health impacts is strong for SPM [2] but many questions remain about how SPM actually affects human health and what makes it particularly harmful. While particle composition is known to play an important role in inducing adverse health effects, much less is known about its role compared to that of particle size and mass. It is therefore important that data obtained from measuring SPM in ambient air is as rich as possible.

This study shows that the PANalytical Epsilon 5 EDXRF is fully capable of analysing particulate matter on air filters according to EPA method IO-3.3. The instrument operates with a high degree of accuracy and precision for a wide range of elements across the periodic table. The non-destructive nature of the method means that it is possible to increase measurement times should an even higher degree of precision be required. Furthermore, samples can be measured repeatedly without damage, ensuring the longevity of standards.

The advantages of the Epsilon 5 are clear. Measurements are accurate and precise and the method benefits from simple, essentially hazard-free, sample preparation. The stability of the instrument is such that individual calibrations can be used for months. As a result, time-consuming re-standardisations are unnecessary and the resulting data are highly consistent over time.

References and Further Reading:

1. UNDP/ESMAP, South Asia Urban Air Quality Management Briefing Note No. 13, 2003: "The Science of Health Impacts of Particulate Matter"

2. UNDP/ESMAP, South Asia Urban Air Quality Management Briefing Note No. 11, 2003: "Health Impacts of Outdoor Air Pollution"

Table 1. Analytical parameters used for the application set up

Elemental range	Secondary Target	kV	mA
Na-K	CaF_2	35	17
Ca-Sc	Ti	70	8.5
Ti-Cr, Ba-Nd	Fe	80	7.5
Mn-Zn, Sm-Pt	Ge	85	7
Ga-Rb, Au-Pb	Zr	100	6
Sr-Y, Bi-U	Mo	100	6
Nb-Mo	Ag	100	6
Rh-Cs	Al_2O_3	100	6

Table 2. Analytical precision for short and long-term measurements

SRM 2783	Si	K	Ti	Cr	Mn	Fe	Cu	Pb
Repeatability (20 consecutive measurements)								
Mean (µg/cm²)	8.704	0.483	0.143	0.018	0.027	2.3186	0.047	0.039
RMS	0.05	0.002	0.005	0.002	0.005	0.0118	0.003	0.005
RMS rel%	0.578	0.473	3.556	9.907	17.408	0.5068	5.759	12.354
Reproducibility (Measurements carried out over 10 days)								
Mean (µg/cm²)	8.704	0.482	0.143	0.018	0.028	2.3267	0.047	0.036
RMS	0.047	0.003	0.007	0.001	0.006	0.0205	0.003	0.003
RMS rel%	0.538	0.601	4.849	5.521	21.731	0.879	6.877	8.948
Counting statistical error								
CSE rel%	0.492	0.446	2.894	5.978	8.153	0.799	4.157	9.109

Table 3. Comparison of measured versus certified values for NIST 2783

SRM2783	Certified (µg/cm²)	Measured (µg/cm²)
K	0.53	0.48
Ca	1.32	1.14
Ti	0.15	0.14
V	0.005	0.005
Cr	0.014	0.016
Mn	0.032	0.018
Fe	2.65	2.32
Ni	0.007	0.007
Cu	0.040	0.043
Zn	0.18	0.18
Ba	0.034	0.025
Pb	0.032	0.030