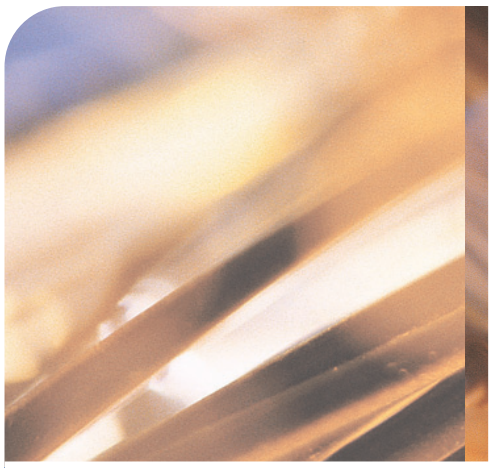


Spectroscopy Focus

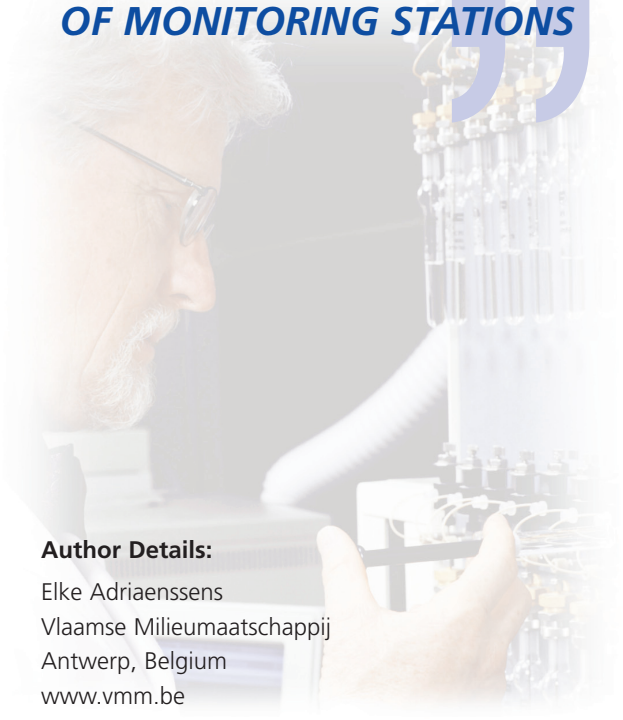
ANALYSIS OF HEAVY METALS IN AMBIENT AIR

Elke Adriaenssens

Exposure to heavy metals causes a range of human disorders and ecological damage. It is therefore vital that emissions are strictly limited and controlled. While heavy metals enter into the environment in a variety of ways, airborne emissions are of particular concern. Once introduced into the atmosphere, pollutants are able to travel great distances from their original source, transferring contaminants to ecosystems far and wide.

To control heavy metal pollution and limit its harmful impacts, governments and regulatory bodies worldwide are implementing increasingly stringent legislation. Meeting these regulations requires highly accurate monitoring techniques. This article looks at the work of Vlaamse Milieumaatschappij (VMM), the Flemish Environment Agency, in monitoring airborne heavy metal pollution in Belgium.

"VMM MONITORS THE QUALITY OF AMBIENT AIR AND OZONE LEVELS THROUGH A NETWORK OF MONITORING STATIONS"



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ABOUT VMM

VMM is a public agency involved in the establishment and implementation of environmental policies in Flanders - one of Belgium's three constitutional regions. Established by decree in 1990, VMM is an independent body with powers of jurisdiction in many aspects of environmental policies. VMM consists of 1052 staff and reports to the Flemish Minister of the Environment.

VMM's mission is to contribute to the realisation of environmental policies to protect water and atmospheric systems, and to monitor the state of the environment. VMM works to achieve these goals in many ways, ranging from the collection and evaluation of environmental data to coordinating the region's participation in international environmental policies.

MONITORING HEAVY METALS IN AMBIENT AIR

Within its many tasks, VMM monitors the quality of ambient air and ozone levels through a network of monitoring stations. VMM also records emission inventories and gives advice concerning environmental permits. The main sources of atmospheric heavy metals are the non-ferrous industry, fossil fuel combustion, waste and traffic. In air, heavy metals occur in breathable, or suspended, dust and also sedimentary dust.

The presence of hazardous substances in ambient air is investigated by various air monitoring networks, measurement campaigns and studies. The main compounds of concern are: sulphur dioxide, nitrogen oxides, ozone, fine dust (PM10 and PM2.5), black fume, VOC (volatile organic compounds), poly-aromatic hydrocarbons, heavy metals (in suspended matter and in deposited dust), acid rain, hydrogen fluoride, dioxins, PCB126 and pesticides in rainwater.

Ambient air measurements usually require verification against default standards. Taking into account sample measurements, calibrations, analyses, validation procedures, processing and assessment - fully validated and interpreted data become available six to nine months after the initial measurement.

VMM'S MONITORING NETWORK

In Flanders, the network of monitoring stations for heavy metals in ambient air (for suspended dust) was established in 1973 and now consists of 25 stations. The network monitors the heavy metal content of fine dust (PM10, this fraction represents 50% of the particles smaller than or equal to 10 µm) for the following metals: Pb, Cd, As, Ni, Zn, Cu, Sb, Cr and Mn.

VMM is also involved in the monitoring of heavy metal deposition. Deposition measurements are concentrated around industrial sites, particularly at non-ferrous and steel industry locations.

Measurement of heavy metal deposition in Flanders started in 1981 and today the network consists of 38 measuring points, 30 of which are located in Hoboken, near Antwerp. For measuring heavy metal deposition, it is the larger particles that are of particular importance.

Figure 2: VMM's samplers: Pourbaix low volume (left) and Leckel PM10 (right)

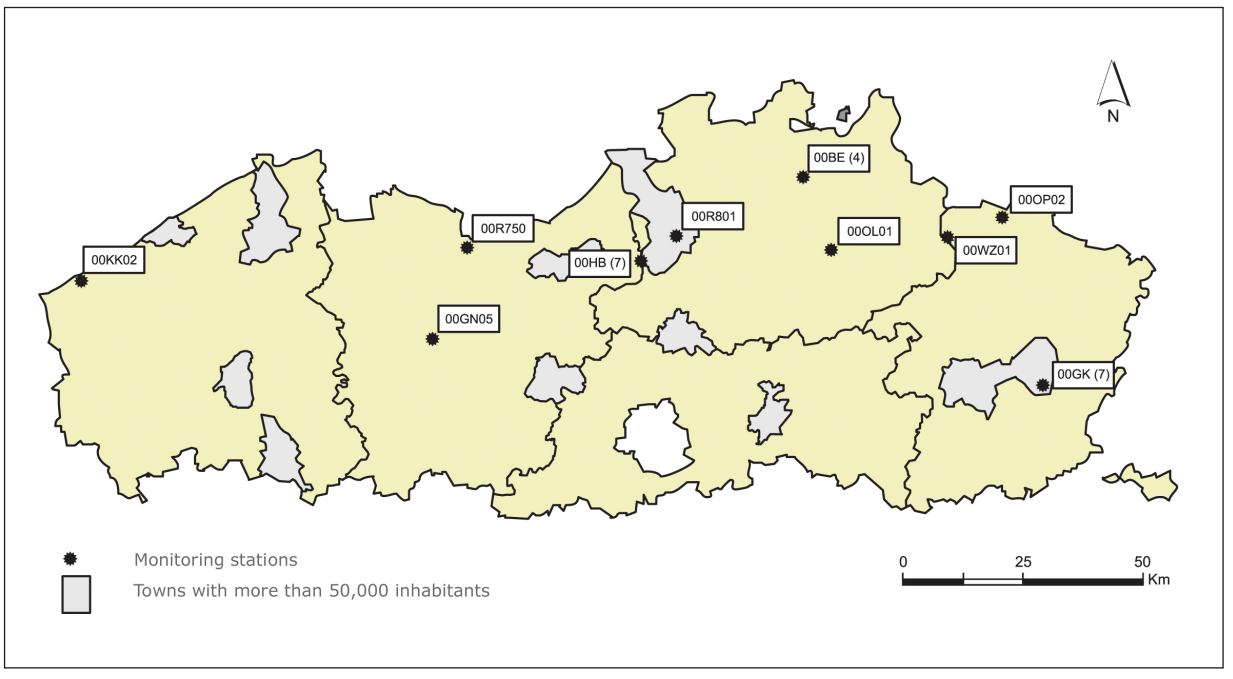

Figure 1: Sampling locations for the determination of heavy metals in ambient air in Flanders

AIR SAMPLING METHODS

Samples are taken at 25 locations throughout Belgium. Prior to 2004, a low volume sampler (Pourbaix) was used at VMM, with a sampling volume of +/- 18 m^3 a day. Air was filtered on a cellulose nitrate filter (50 mm diameter, 0.45 µm pore size) at fractions between PM10 (fine dust) and TSP (total suspended particles). Sampling equipment has been updated and Leckel PM10 samplers with quartz filters (47 mm diameter, 0.45µm pore size) are now used.

The VMM network employs two sampling routines: at some locations sampling is conducted on a daily basis (55 m^3 sample volume per day); at other locations weekly sampling is performed (168 m^3 sample volume per week).

PREPARATION OF STANDARDS

VMM produces its own standards, as none are commercially available for either sampler system. To generate standards, a nebulizer is used to form an aerosol with 400 ml of a standard solution for 200 minutes.

The aerosols are collected on a blanco filter and analysed by X-ray fluorescence spectrometry (XRF). After dissolution in a microwave, samples are analysed by F-AAS and GF-AAS. They are then ready for use as standard concentrations for the XRF software.

ANALYSIS OF HEAVY METALS BY XRF SPECTROSCOPY

At VMM, both energy dispersive X-ray fluorescence (EDXRF) and wavelength dispersive X-ray fluorescence (WDXRD) spectrometry are used to analyse heavy metals in ambient air. Accurate and precise monitoring of heavy metals is essential to keep pace with ever more demanding legislation.

Table 1: Target values for As, Cd, Ni and the limit value for Pb, according to EU directives

Parameter	EU target/limit value (ng/m^3)	Entry in force
As	6	31/12/2012
Cd	5	
Ni	20	
Pb	500	01/01/2005

For example, *Table 1* shows the low limits and target values required under the latest EU directives for some important heavy metal pollutants.

Until 2005 VMM used only the WDXRF technique to analyse sample filters loaded with heavy metals. Now the agency uses both WDXRF and also polarised EDXRF for this purpose:

HEAVY METAL ANALYSIS BY WDXRF

At VMM, a PW 2400 WDXRF spectrometer (PANalytical, www.panalytical.com) equipped with an Rh tube is used to measure As, Cu, Cr, Mn, Ni, Pb and Zn. The spectrometer is equipped with a Cr tube for the analysis of Cd and Sb. Measurement time for the Rh tube is 12 minutes per sample. Measurement time with a Cr tube is 3 minutes per sample.

Table 2 shows the analysis characteristics of WDXRF spectrometry. A major advantage of this technique is that samples do not need any sample preparation prior to analysis - unlike most other methods for heavy metals analysis. Furthermore WDXRF is non-destructive, very rapid and inexpensive in terms of cost per analysis.

In this situation, however, WDXRF does require that laboratory personnel perform sample analysis twice; first with the Rh tube and then with the Cr tube.

VMM manage this by first analysing sample filters for one year with the Rh tube and then re-analysing the filters after installing the Cr tube. This delays the availability of results and duplicate analyses have an impact on the filter material.

Table 2: Analysis characteristics of the PW2400 WDXRF spectrometer

	Range (ng/m^3)	Line	Detection limit (ng/filter)	Detection limit (ng/m^3) Pourbaix (18m^3/day)	Leckel (55m^3/day)
As	33-1000	K,	500	33	9.1
Cd	4-1000	L·	60	4	1.1
Cr	20-1000	K·	300	20	5.4
Cu	67-6700	K·	800	53	14
Mn	10-1000	K·	150	10	2.7
Ni	20-1000	K·	250	17	4.5
Pb	50-13300	L,1	400	27	7.3
Sb	4-1000	L·	60	4	1.1
Zn	17-10000	K·	150	10	2.7

HEAVY METAL ANALYSIS BY EDXRF

EDXRF analysis at VMM is carried out on an Epsilon 5 polarised EDXRF system (PANalytical, www.panalytical.com). Equipped with a Gd tube, the spectrometer has been specially developed for low-level determination of heavy elements.

Samples are measured for 30 minutes. *Table 3* shows the analysis characteristics of the Epsilon 5. It clearly demonstrates lower detection limits for As, Ni and Pb compared to WDXRF data. Detection limits for all three elements were even lower than the limit and target values specified in the EU directive.

The same advantages as for WDXRF apply to the EDXRF method, including simple sample preparation, non-destructive testing, speed and relatively low costs.

Furthermore, analysis has no impact on the filter material and all parameters are obtained in one analysis run.

EDXRF analysis shows higher detection limits for Cd and Sb in comparison with WDXRF and the detection limit for Cd is identical to the target limit in the EU directive, which means that EDXRF cannot be used for Cd analysis at this time.

Table 3: Analysis characteristics obtained with the Epsilon 5 polarised EDXRF spectrometer

	Range (ng/m^3)	Target	Detection limit (ng/filter)	Detection limit (ng/m^3) - Leckel 55m^3/day	168m^3/day
As	1-360	KBr	50	0.91	0.30
Cd	9-550	CsI	275	4.98	1.64
Cr	2-550	Co	100	1.81	0.60
Cu	5-1800	Ge	175	3.17	1.04
Mn	2-360	Co	100	1.81	0.60
Ni	5-360	Ge	150	2.72	0.89
Pb	9-5500	Zr	360	6.52	2.14
Sb	9-550	CeO2	400	7.25	2.38
Zn	5-5500	Ge	275	4.98	1.64

CONCLUSION

VMM has found that a combination of WDXRF and EDXRF spectrometry enables highly accurate analysis of airborne heavy metals at industrial locations. Measurements are first carried out with EDXRF for all parameters, and thereafter WDXRF analysis is used for Cd and Sb.

XRF is a valuable technique for the analysis of heavy elements in suspended matter, supported by the demonstration of equivalence with AAS or ICP-MS reference methods.

Elke Adriaenssens is working within the air monitoring network of the Flemish Environment Agency. She is responsible for lab activities concerning the semi-automatic measurements

Exclusive Agreement Announced

Aspectrics, Inc the innovator of Encoded Photometric Infrared (EP-IR) analysers announces that it has entered into an exclusive agreement with Thermo Fisher Scientific to seamlessly integrate Thermo Scientific GRAMS spectroscopy software with Aspectrics' groundbreaking Encoded Photometric Near Infrared (EP-NIR) process analysers. Jim Yano, Vice President of marketing for Aspectrics comments: "Our collaboration with Thermo Fisher Scientific demonstrates Aspectrics' commitment to customer satisfaction and development within the global market. With Thermo Fisher Scientific's rich heritage in spectroscopy software and Aspectrics' groundbreaking EP-NIR technology, this combination will result in a complete real-time process analyser solution that will enable our customers to achieve faster and more reliable analyses."

Aspectrics' EP-NIR analysers offer a more efficient alternative to traditional NIR systems, with a spectral range extending further than the common 2100nm and achieving a range of 1375-2750nm. The patented Encoder Disk technology provides ultra fast sampling capability (100 Hz) for multi component analysis in a process rugged design to meet the demand for the process monitoring industry. Thermo Scientific GRAMS is a spectroscopy software solution used by industry professionals worldwide for visualising, processing and managing data from FT-IR, NIR, Raman, UV-Vis, Fluorescence, NMR and hyphenated instruments manufactured by multiple vendors.

"We are excited to be working with Aspectrics," said David Champagne, Vice President and General Manager of informatics at Thermo Fisher Scientific. "Aspectrics' innovative EP-NIR technology seamlessly integrates with GRAMS, an open standards platform from which Aspectrics's clients can control and integrate data from multiple instruments from multiple vendors." Aspectrics' EP-NIR analysers recently received an 'honorable mention' in the Editors' Award at Pittcon® 2007, the largest North American conference and exposition on laboratory science and instrumentation.