

**CO-ORDINATED RESEARCH PROGRAMME
ASSESSMENT OF LEVELS AND HEALTH-EFFECTS OF AIRBORNE
PARTICULATE MATTER IN MINING, METAL REFINING AND METAL
WORKING INDUSTRIES USING NUCLEAR AND RELATED ANALYTICAL
TECHNIQUES**



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**WORKPLACE MONITORING AND OCCUPATIONAL HEALTH STUDIES IN
THE ŠOŠTANJ THERMAL POWER PLANT, SLOVENIA**

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WORKPLACE MONITORING AND OCCUPATIONAL HEALTH STUDIES IN THE ŠOŠTANJ THERMAL POWER PLANT, SLOVENIA

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Up to now, only a few investigations have been performed in the Šoštanj Thermal Power Plant (TPP) involving comprehensive studies of trace elements, toxic elements, heavy metals and radionuclides in the workplaces. The aim of the project is development and application of nuclear and nuclear-related analytical techniques for workplace pollution and occupational health studies, leading to formation of a database concerning the trace element air pollution inside the Šoštanj Thermal Power Plant. In this report, the emphasis is on the methodology and analytical development (neutron activation analysis, X-ray spectrometry, total-reflection X-ray fluorescence (TXRF) spectroscopy and proton induced X-ray emission (PIXE)), and to a lesser extent on the results obtained up to now. Analytical results for several certified reference materials of similar matrix as the real samples investigated were obtained. Results obtained by the k_0 -standardization method and XRF technique for aerosols (coarse and fine fractions) are also presented and discussed.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

The general scope of the project is a better knowledge of the state of air pollution in the Šoštanj Thermal Power Plant by performing workplace monitoring and occupational health studies involving determination of trace element air pollution from industrial emissions by analysing airborne particulate matter (APM) and biological samples taken from exposed workers.

Energy production from fossil fuel pollutes the workplace, the surrounding environment and also, because of the use of ash and gypsum in civil engineering, the living environment. Underground lignite mining results in high amounts of coal fly ash and radon productions. Use of the ventilating system produces high values of ash and radon in the environment. Coal, after drying on the tips, is transported to the TPP on beltways which cause large amounts of coal dust to be dispersed into the environment.

The Šoštanj Thermal Power Plant with an installed electric power capacity of 745 MW consumed 3,8 million tons of lignite coal in the year 1992. This represents 90% of the total coal mine production, of which it is estimated only 32% is used effectively. The sulphur content of the coal is 1.3%. The SO₂ emission factor in the TPP is 0.85; the emissions in the year 1992 were 94,120

tons of SO₂ (without desulphurization), 6,085 tons of fly ash, 9,009 tons of No_x and unknown quantities of other pollutants. The SO₂ concentration in the flue gases is 3 to 8 gm⁻³ and of No_x 0.2 to 0.6 gm⁻³. A schematic diagram of the plant is shown in Fig. 1. Yearly ash production is up to 800,000 tons. The ash disposal site has a surface of 0.5 km². Part of this surface is covered with grass while the rest flooded with water.

In the some yearly periods (late autumn, winter and early spring) the workplaces are contaminated not only by ash and coal dust but also with high concentration of organic pollutants. After coal is burned in the furnace system of the TPP, the elements contained in coal separated into two major fractions; those which are volatile and are transported with flue gases, and those which mainly remain in the ash or fume slag. The passage of trace metals through the boiler to the stack is mainly dependent on the combustion temperature, the residence time of the ash in the hot combustion zone of the boiler and the efficiency of the electrostatic precipitators. Higher temperatures and longer ash residence times favour the evaporation of volatile trace metal compounds from the ash (coal). Slag tap boilers (combustion temperature around 1973 K, residence time 1-2 h) normally show higher enrichment ratios for smaller particles, which preferentially pass the electrostatic precipitations, than do dry bottom boilers (combustion temperature around 1625 K, residence time 2-5 s). Šoštanj TPP is a dry bottom boiler (BABCOCK). During combustion, through the volatilization and subsequent condensation mechanism during flue gas cooling to 450 K, before exhaust to the atmosphere, some elements are enriched (10 to 40 times) [12] in the finest size fractions.

Workers at the Thermal Power Plant in some sectors are exposed to high levels of coal dust, in others to dusty operations with ash and electrostatically precipitated fly ash, and in addition a force of welders is employed for maintenance and construction tasks. Contact with coal and fly ash lead to wear of milling and transporting devices. To keep these devices in operation they must sometimes be repaired by welding with a special metal alloy which has a high content of heavy metals. Welders work 5 to 6 hours per day (50 m of weld) and they are protected only from UV light. They are exposed to high concentration of metals in the inhaled welding fume. In the particular working conditions sometimes welders are exposed to high concentrations of fume. In some cases other workers are exposed to coal dust; other are exposed to very high concentrations of fly ash. The major pollutants of concern in ash and coal are quartz particles, natural radioactive radionuclides from the ²³⁸U chain (the ash contains 25-30 mg/kg uranium), polycyclic aromatic hydrocarbons, heavy metals and other toxic microelements.

It is the goal of the project that on its successful completion, an improvement in the development and applications of nuclear and nuclear-related analytical techniques will be achieved, and a database concerning trace element air pollution in the TPP will be obtained, possibly leading to appropriate decisions in environmental control. Particular research objectives are:

1. To improve and further develop analytical techniques for multielement characterization of the materials analysed, including speciation of some particular pollutants (e.g. Hg, Cr).
2. To determine the actual exposure of the three critical groups of workers (those exposed to coal dust, those exposed to coal ash and welders).
3. To carry out a programme of health checks on the exposed workers.
4. Following a preliminary evaluation of 2. and 3., to prepare, carry out, and monitor technical solutions for reducing exposure, improving working conditions and evaluating and monitoring the health status of the critical groups.

Close collaboration has been established between the Jožef Stefan Institute, its associated partner ERICo Velenje (**E**cological **R**esearch & **I**ndustrial **C**ooperation), the Institute for Occupational Health, Traffic and Sport, Ljubljana and with the Idria Mercury Mine (now closed). ERICo is giving us assistance in collecting and analysing aerosols, and the Institute for Occupational Health, Traffic and Sport, Ljubljana, is contacted on behalf of the Šoštanj TPP.

2. METHODS

2.1. Sample collection

To perform the planned programme in the Šoštanj TPP, 10 sampling workplace sites were chosen. Five of them were exposed to high concentration of coal dust and five with ash. The sampling sites were chosen at the following workplaces:

- The boiler bunkers, Block 5, exposure - coal
- The internal transport of ash, Block 4, exposure -ash
- The internal transport of ash, Block 5, exposure - ash
- The boiler bunkers, Block 4, exposure - coal
- Control of the coal transportation system PE-24, exposure - coal
- Internal transport of ash, Block 2, exposure - ash
- The boiler bunker, Block 1-3, exposure - coal
- The external transport of ash, Block 1-3, exposure - ash
- Control of the coal transportation system PE-05, exposure - coal
- First repeated reheater unit PP1, Block 5, exposure -ash.

Aerosols are collected by means of an in-house constructed single jet sampler [1], with a cut-off point of $\sim 2.5 \mu\text{m}$. The sample inlets are positioned 1.8 m above the ground. The fraction ~ 2.5 to $10 \mu\text{m}$ is collected on a Nuclepore polycarbonate membrane filter (37 mm diameter, pore size $0.45 \mu\text{m}$), with free air flow reduced to a diameter of 13 mm in order to achieve a higher concentration of coarse particles in the central part of the filter. The particulate fraction finer than $\sim 2.5 \mu\text{m}$ is collected on a Nuclepore

polycarbonate membrane filter (47 mm diameter, pore size 0.45 μm). Both filters are held in the original Nuclepore holders. The air flow rate through the separator and both filters is regulated by a critical orifice between the filters and a GAST oil-less diaphragm vacuum pump (type DOA). The flow rate is not constant and it decreases by up to 50% from the beginning to the end of the sampling period. The arithmetic median value of the flow rate is about 400 L·h⁻¹, representing approximately one third of the rate of human breathing. The flow rate is measured by a rotameter at the beginning of sampling, checked every second day and finally at the end of the sampling period. The effectiveness of the separator in defining the two fractions was controlled by examination of the collected particulates under a scanning electron microscope (LEITZ - AMR); no evidence for collection of particles greater than 2.5 μm in the fine fraction was ever found. Sampling times vary, depending on the minimal flow rate necessary for successful operation of the separator and determination of the content of air particulates, being from 3 to 14 days.

2.2. Sample preparation

The procedure for samples to be analysed by instrumental neutron activation analysis is as follows:

Two-hundred milligram aliquots of SRMs are packed in polyethylene ampoules (Kartell, Noviglio, Italy), together with an Al-0.1% Au alloy wire (Central Bureau for Nuclear Measurements, Geel, Belgium) of 1.0 mm diameter and a 0.125 mm Zr foil (Goodfellow, Cambridge, UK), which serve as comparator and fluence rate monitors.

APM loaded filters are pelletised with a manual press (Mod. 25011, Specac, UK) in a pellet die of 5 mm diameter and packed the same way as SRMs.

The procedure for samples to be analysed by energy dispersive X-ray fluorescence spectrometry is as follows:

Loaded filters are weighed on a Mettler balance AE 163 having a precision of 10 μg (Mettler Instrumente AG, Switzerland), after neutralising the charge with a Nuclepore static eliminator (Nuclepore, Cambridge, USA). Filters are kept in Petri dishes prior to analysis.

2.3. k_0 -based instrumental neutron activation analysis (INAA)

All irradiations are made in the channels of the TRIGA Mark II reactor of the Jožef Stefan Institute (IJS): for short irradiation (from 2 to 5 min) in the pneumatic tube at a thermal flux of $3.5 \cdot 10^{12}$ neutrons·cm⁻²·s⁻¹, and for longer irradiations in the carousel facility at a thermal neutron flux of $1.1 \cdot 10^{12}$ neutrons·cm⁻²·s⁻¹ (irradiation time for each sample was 18-20 h). After irradiation the samples are transferred to clean 5 ml polypropylene mini scintillation vials (Atom Medical Ltd., Hove, UK) for measurement. The radionuclides used in the determination of up to 50 elements in each sample,

their half-lives and gamma-energies measured are given elsewhere [2]. The samples are measured on two HP Ge detectors (Ortec, USA) with 17 and 20% relative efficiencies [18] which are connected to a Canberra Series 90 multichannel analyser (Canberra Packard, USA), and a new detector (also manufactured by Ortec) with 40% relative efficiency connected to a Canberra S 100 multichannel analyser. For the k_0 standardization method we need absolutely calibrated detectors [18]. For short half-life nuclides samples are measured 90 seconds and 2.5 hours, and for medium and long-lived nuclides 2 days, 8 days and 15 days after the end of irradiation. Measurements are performed at such a distance that the dead time is kept below 10% and random coincidences are negligible. The Au comparators are measured at a large distance (i. e. 16 - 20 cm) and their geometry is approximated by a small cylinder. The Zr foil is measured in the form of discs, and, again, the dead time is kept below 10%. Spectra are processed by the SAMPO 90 program [3]. Effective solid angle calculations are made using the SOLANG program [4]. Elemental concentrations are calculated by the ROMOS program [5]. The relevant nuclear constants (i. e. k_0 , Q_0 factors, etc.) are taken from the literature [6-9]). At this moment we have installed a new software packet KAYZERO[®]/SOLCOI[®] which includes the above two steps [17].

2.4. Energy dispersive X-ray fluorescence spectrometry (EDXRF)

Samples are placed on an in-house constructed automatic sample changer carousel facility with a capacity of 10 specimens. Two different set-ups are used for EDXRF analysis: (i) a 1 GBq ¹⁰⁹Cd excitation source (Isotope Products Laboratories, Burbank, USA) and a Si(Li) detector (Canberra Industries, Meriden, USA) with an active area of 30 mm², thickness of 3 mm and FWHM of 165 eV at 5.9 keV coupled to a Canberra S 100 multichannel analyser (MCA); (ii) a 1 GBq ²⁴¹Am excitation source or a 1.8 GBq ⁵⁵Fe source (both supplied from Isotope Products Laboratories) and a low energy Ge detector (Canberra Industries) with an active area of 30 mm², thickness of 5 mm and FWHM of 140 eV at 5.9 keV. Spectra are processed and quantitative analysis performed using AXIL-PC and QAES (Quantitative Analysis of Environmental Samples) software (Canberra Industries). Both systems were calibrated using NIST SRM 1832 XRF Thin Film Standards for Al, Si, Ca, V, Mn, Co, and Cu, and NIST SRM 1833 XRF Thin Film Standards for Si, K, Ti, Fe, Zn, and Pb.

2.5. Total-reflection X-ray fluorescence (TXRF)

Total reflection XRF spectroscopy is an analytical technique which is characterised by a few orders of magnitude better sensitivity than conventional X-ray fluorescence spectroscopy. The technique is based on the total reflection of the incident excitation beam from the sample substrate which is usually an optically polished quartz plate. The excitation beam must be well collimated in order to be able to adjust for as possible part of the beam the incident angle of few *mrad*, what is usually the value of the critical angle for X-rays of energy around 20 keV.

The TXRF system is assembled using an X-ray spectrometer, a tube excitation system and the total reflection module. The X-ray spectrometer is based on a Si(Li) detector (EG & G Ortec, 30 mm² x 3 mm sensitive volume, 25 μm Be window), with a resolution of about 170 eV at 5.9 keV. The electronics system (Canberra), consists of a fast spectroscopy amplifier M 2024, M 8075 ADC, an M 3105 power supply and an S-100 PC based MCA. This system contains pile up rejection (PUR) circuitry, which has proved indispensable for data acquisition involving the high counting rates needed when the dead time exceeds 10% [20].

The TXRF technique has proved to very successful in the environmental analysis of rain water, river water and sea water, but it can also be applied in atmospheric chemistry for aerosol analysis [21].

2.6. Particle induced X-ray emission (PIXE)

In atmospheric pollution studies, ion beam analysis using accelerators has found a number of successful applications since the early 1970s. Among them, particle induced X-ray emission (PIXE) has gradually developed into a standard tool in this field; the application of PIXE to atmospheric research makes use of all its advantageous features. Routine PIXE analysis can be performed with quite a simple electrostatic accelerator that requires only a minimum of technical assistance. The high X-ray production cross-sections for elements with Z values between 10 to 90, and at the same time low contributions to the X-ray spectral background, mainly due to the bemsstrahlung of secondary electrons in the sample matrix, make PIXE a very sensitive analytical tool compared with other nuclear and atomic spectrometric techniques; relative detection limits, for the majority of elements above Al, are of the order of 10⁻⁵ - 10⁻⁷. The best overall performance is attained by using light ions, especially 2-3 MeV protons.

The experimental conditions of the PIXE measurements were as follows: a proton beam energy of 1.39 MeV and a proton current of ≈ 10 nA that was diffused by a gold foil to make it more homogeneous. The proton dose on each target was preset at 5 μC. The beam spot was 5 mm x 5 mm. The X-ray detector was an intrinsic HPGe detector with an 8 mm Be window. The detector had an area of only 25 mm² and the resolution achieved was 145 eV at 5.9 keV. Spectrum analysis was performed by the AXIL program [22] and quantitative analysis was based on a computer program developed in the laboratory. The calibration for quantitative analysis utilised measurements on a thin sample prepared by applying a known amount of a multielement standard solution, containing a set of elements (K, Ca, Cr, Fe, Ni, Zn, As, Br, Rb, Sr and Pb) to a Mylar foil on an area smaller than the proton beam. The absolute load of elements did not exceed 0.3 mg.

3. RESULTS AND DISCUSSION

The concentrations of dust in air was several higher at the workplaces than in the unloaded environment. In enclosed places below the electrostatic filters the concentrations were extremely high but not higher than the values suggested by WHO as limit values. In the boiler, after the heating process was stopped, concentrations of aerosols in air were extremely high and exceeded the permissible values. Beside that, some elements have an affinity for the respirable fraction of dust, leading to high occupational exposure at the workplace from heavy metals in respirable particles, which have a dominant effect on the workers' health.

Concentrations of elements in the respirable fraction of aerosols, coming from coal fly ash and coal dust at selected workplaces, are shown in Table 1 and Table 2, respectively. All results were obtained using the XRF technique. A comparison between these workplace areas in the Šoštanj TPP and an urban area near Šoštanj is presented in these Tables, as well as the limiting concentrations for workplaces defined by local law [23] and WHO [24].

In 1994, much effort was put into quality assurance. Thus, as well as the analysis of IAEA Lichen research material and the APM collected on filter media (prepared by S. Landsberger), some other standards (SRMs) or certified reference materials (CRMs) were analysed by the proposed methods/procedures. The analytical results for several NIST SRMs, namely SRM No. 1633a Coal Fly Ash, SRM No. 1570 Spinach, SRM No. 3087 Metals on Filter Media, and for BCR CRM No. 128 Fly Ash on Artificial Filter are presented in [15]. The results for NIST SRM No. 1643c Trace Elements in Water are presented in Ref. [16].

The results are reported as arithmetic means of several independent determinations with uncertainty values as 95 % confidence intervals, combined in quadrature with an additional 3.5% estimated systematic error as reported by De Corte [10] for the overall average uncertainty for k_0 - standardization NAA. In these two tables certified values and "consensus" values as defined by Gladney et al. [11] for the elements determined are also given.

Table 1. Concentration of elements in the respirable fraction of aerosols coming from coal fly ash ($\mu\text{g m}^{-3}$) [19].

| | Sampling sites | | | PE-24 | PE-05 | Block 1-3 | Block 4 | Block 5 |
|------|-------------------------|---------------|-------|--------------|--------------|------------|------------|------------|
| | Limiting concentrations | | | Coal control | Coal control | Bunkers | Bunkers | Bunkers |
| | Workplace | Urban area | | 1992-05-21 | 1992-06-02 | 1992-05-29 | 1992-05-18 | 1992-04-29 |
| WHO | | Average Škale | | | | | | |
| Mass | 10000 | 50 | 31 | 1220 | 2290 | 5090 | 860 | 960 |
| Al | | | 0.246 | 29 | 50.2 | 26.7 | 36.8 | 38.6 |
| Si | | | 0.333 | 72.7 | 119 | 60.1 | 94.7 | 97.4 |
| S | | | 1.814 | 15.2 | 16.7 | 12.3 | 15.1 | 14.1 |
| Cl | 2000 | | 0.024 | 2.77 | 8.94 | 2.06 | | 0.69 |
| K | | | 0.141 | 6.93 | 11.1 | 6.02 | 9.04 | 7.02 |
| Ca | 5000 | | 0.157 | 29.5 | 36.3 | 18.2 | 29 | 17.4 |
| Ti | 10000 | | 0.011 | 1.44 | 2.27 | 1.03 | 1.71 | 1.6 |
| V | 100 | 1 | 0.003 | | 0.13 | 0.36 | | |
| Cr | 1000 | 1 | 0.003 | | | | 0.32 | |
| Mn | | 1 | 0.015 | 0.37 | 0.86 | 0.22 | | 1.29 |
| Fe | 10000 | | 0.164 | 28.3 | 46.2 | 16.9 | 30.9 | 24 |
| Co | 100 | | | | 0.25 | | | 1.19 |
| Ni | 500 | 1 | 0.006 | | | | | 0.42 |
| Cu | 1000 | | 0.004 | | | 0.03 | 0.15 | 0.12 |
| Zn | 5000 | | 0.038 | 0.66 | 0.61 | 0.35 | 0.48 | 0.27 |
| Pb | 150 | 0.5 | 0.045 | 0.39 | 0.49 | 0.12 | 0.45 | |
| Rb | | | | 0.15 | 0.13 | 0.07 | 0.19 | 0.36 |
| Sr | | | 0.006 | 0.19 | 0.31 | 0.1 | 0.18 | 0.26 |
| Y | 1000 | | | | 0.04 | | | 2.24 |
| Zr | 5000 | | 0.004 | 0.09 | 0.87 | 0.03 | | |
| Nb | | | | 0.08 | | | | |
| Mo | 5000 | | | 0.07 | 0.04 | | 0.08 | |
| Ga | | | | | | | | |
| Br | 700 | | 0.007 | | | | | |
| U | 50 | | | | | | | |

Table 2. Concentration of elements in the respirable fraction of aerosols coming from coal dust ($\mu\text{g m}^{-3}$) [19].

| | Sampling sites | | | Block 2 | Block 1,2,3 | Block 4 | Block 5 | Block 5 |
|------|-------------------------|------------|---------------|--------------------|-----------------|--------------------|--------------------|--------------|
| | Limiting concentrations | | | Internal transport | Pumping station | Internal transport | Internal transport | PP1 reheater |
| | Workplace | Urban area | | 1992-05-29 | 1992-06-02 | 1992-05-07 | 1992-05-12 | 1992-10-30 |
| | | WHO | Average škale | | | | | |
| Mass | 10000 | 50 | 31 | 7 | 96 | 450 | 310 | 34500 |
| | | | | 70 | 68 | 4880 | 3290 | 304000 |
| Al | | | 0.246 | | 0.006 | 12.2 | 10.3 | 2370 |
| Si | | | 0.333 | 0.2 | 0.56 | 29.7 | 31.3 | 6230 |
| S | | | 1.814 | 1.91 | 2.86 | 6.3 | 6.75 | 1070 |
| Cl | 2000 | | 0.024 | 0.46 | | | | |
| K | | | 0.141 | | 0.3 | 3.42 | 3.92 | 1080 |
| Ca | 5000 | | 0.157 | 0.26 | 2.49 | 13.5 | 16.9 | 1420 |
| Ti | 10000 | | 0.011 | 0.009 | 0.03 | 0.7 | 0.64 | 145 |
| V | 100 | 1 | 0.003 | 0.005 | | 0.01 | 0.008 | 5.16 |
| Cr | 1000 | 1 | 0.003 | | | | | 4.1 |
| Mn | | 1 | 0.015 | | | | | 45.5 |
| Fe | 10000 | | 0.164 | 0.26 | 0.48 | | | 5620 |
| Co | 100 | | | | | | | 28.3 |
| Ni | 500 | 1 | 0.006 | | 0.01 | | | 3.72 |
| Cu | 1000 | | 0.004 | | | | | 5.25 |
| Zn | 5000 | | 0.038 | 0.02 | 0.05 | | | 113 |
| Pb | 150 | 0.5 | 0.045 | 0.05 | 0.07 | | | 29.1 |
| Rb | | | | | 0.02 | | | 16.5 |
| Sr | | | 0.006 | | | | | 27.7 |
| Y | 1000 | | | | 0.03 | | | 27.7 |
| Zr | 5000 | | 0.004 | | | | | 11.3 |
| Nb | | | | | | | | 1.83 |
| Mo | 5000 | | | | | | | 6.52 |
| Ga | | | | | | | | 4.52 |
| Br | 700 | | 0.007 | | | | | 0.18 |
| U | 50 | | | | | | | 1.92 |

Concerning the quality control of the results by k_0 -INAA, or NIST SRM 1633a Coal Fly Ash, 32 elements were quantitatively determined. The concentrations obtained for 12 out of 13 of the elements were statistically indistinguishable from the certified values. For the remaining 19 elements, for which no certified values exist, 18 experimentally obtained values were statistically indistinguishable from the "consensus" values. For Br, only 1 value was found in the literature, so no reliable comparison could be made.

Since the ED XRF technique requires demanding preparation of the target and a knowledge of the attenuation of excitation and fluorescence rays in the sample when thick targets are applied, this analytical tool was used only for thin (i. e. filter) samples.

The results obtained are presented in Ref. [15]. Since the values quoted in the certificate of analysis for the NIST SRM 3087 Metals on Filter Media (see Table 4 in Ref. [15]) are in $\mu\text{g}/\text{filter}$, the same unit is used for the results of our analyses. Uncertainties are expressed as two standard deviations, in order to be comparable with the certificate, where they are also quoted in the same way. In addition, the certified values are also expressed in $\mu\text{g}\cdot\text{cm}^{-2}$, to be comparable with the results for the other CRMs. It is evident from Table 4 (Ref. [15]) that for all 9 elements certified no statistical difference between the certified and experimentally obtained values could be found, with the exception of Mg, which was below the detection limit (a vacuum should be applied to the system in order to determine this element).

A summary of the analytical results by ED XRF for BCR CRM No. 128 Fly Ash On Artificial Filter is given in Ref. [15]. It can be seen that for 5 elements out of the 10 certified and for one among the 4 elements which are not certified, quantitative data were obtained. Unfortunately, only the data for Fe and Zn can be accepted as analytically reliable, with uncertainties of 5.5 % and 10 %, respectively. For the other 4 elements Cu, Mn, Ni and Pb, the experimentally obtained uncertainties are unacceptable, ranging from 44 % for Pb to 77 % for Ni. When comparing elemental values in surface density units, $\mu\text{g}\cdot\text{cm}^{-2}$, for NIST SRM 3087 and BCR CRM No. 128, it could be noticed that the loadings for the first SRM are approximately two orders of magnitude higher than for the latter one. For the elements As, Cd, Co, Cr, Hg, Th and V in BCR CRM No.128, the mass fractions on the loaded filter are below the detection limit of the method applied, and it can be concluded that a loading of roughly $0.1 \mu\text{g}\cdot\text{cm}^{-2}$ per element is required for quantitative analysis using our ED XRF system.

Using the k_0 -standardization method of NAA as implemented in this study, 50 elements can in principle be determined from a single irradiation. In real samples, quantitative data for approximately 30 elements could realistically be expected, with the elemental values statistically indistinguishable from certified ones (20 out of 21 as presented in Ref. [15]). Using an additional short irradiation (i.e. 5 min), data for an additional 12 elements could be obtained (Al, Cl, Cu, Dy, I, Mg, Mn, Ni, Si, Ti, V, Y). It is well known that Pb cannot be determined by NAA at $\mu\text{g}\cdot\text{g}^{-1}$ level, and some other

technique (including ED XRF) should be applied for analysis of this heavy metal.

Using ED XRF with the set-up described, up to 20 elements having $Z \geq 13$ were usually sought: (i) Si, P, S, K, Ca, Ti and V using an ^{55}Fe exciting source connected to a low energy HP Ge detector, (ii) Cr, Mn, Fe, Ni, Cu, Zn, Pb, Br, Sr and Zn using a ^{109}Cd exciting source connected to a Si(Li) detector, and (iii) Cd, Sb and Ba using a ^{241}Am exciting source connected to a low energy HP Ge detector. This method is much faster than INAA, requiring less than two hours per measurement, thus allowing a throughput of about 60 samples per week when using a sample changer and two detectors. It is suitable for processing a large number of samples of similar matrix composition such as APM collected on filters; however, the quantity of air sampled should be such as to allow elemental surface densities of approximately $0.1 \mu\text{g}\cdot\text{cm}^{-2}$ in order to ensure acceptable quantitative analysis.

Both techniques are currently being implemented for the analysis of biological samples, lichens as biomonitors for air pollution, and for the analysis of APM collected by an in-house constructed single-jet APM separator [1], in the framework of the air pollution survey on the workplaces. On the basis of experience obtained in implementing both methods, ED XRF was chosen for the analysis of APM, and the INAA procedure as a control method for APM, as well as for the analysis of bulk precipitation and lichens. The APM separator used is working at an average flow-rate of $0.4 \text{ m}^3\cdot\text{h}^{-1}$ for up to 14 days, collecting up to 1 mg APM cm^{-2} , which allows quantitative determination of 15 elements, on average, including Si, S, Ni, Cu and Pb, thus representing elements complementary to the INAA data. Some preliminary results concerning air pollution obtained by measuring trace elements in APM and bulk precipitation have already been published, and the details can be found elsewhere [12-14].

4. PLANS FOR FUTURE WORK

It is planned to continue systematic trace element air pollution monitoring and research in the workplaces of the Šoštanj thermal power plant using nuclear and nuclear-related analytical techniques. Airborne particulate matter and biological samples taken from occupationally exposed humans will be systematically analysed.

The group of workers who are exposed to dust is relatively small. For such studies and for comparison with previous results on the negative health effect on workers we need to extend the number of persons in the group. If we, as a group in the IAEA project have the same or similar programme as the groups from other countries involved in the coordinated project we could have a larger sample and also be able better to predict health effects on persons in the workplace.

Thus the aim of our programme is:

1. Sampling two dust fractions, separated by aerodynamic diameter into a fine fraction (0-2.5 μ m) and a coarse fraction (2.5-10 μ m),
2. Use of a Casella personal sampler with centrifugal separator facility and also other sampling devices for comparison.
3. To determine the mass fractions of dust based on the gravimetric method.
4. To determine elemental concentrations with various methods (EDXRF, TXRF, PIXE, k_0 -INAA).
5. To determine concentrations and speciation of highly toxic elements in the dust (Cr³⁺ and Cr⁶⁺).
6. To determine concentrations of organic pollutants using different methods of sampling and analytical techniques.
7. To determine element concentrations in appropriate human biological samples based on medical advice.

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REFERENCES

- [1] STROPNIK, B., BYRNE, A. R., SMODIŠ, B., STEGNAR, P., "Chemical composition of airborne particulate matter (APM) in the Šaleška Valley, Slovenia, World Clean Air (Proc. 9th Congress, Atmospheric Chemistry, Montréal, 1992), Vol.2, Air & Waste Management Association, Pittsburgh (1992) IU-7.08.
- [2] SMODIŠ, B., JAČIMOVIĆ, R., STEGNAR, P., JOVANOVIĆ, S., Multielement analysis of NIST proposed SRM 1547 Peach Leaves, J. Radioanal. Nucl. Chem., Articles **160** 1 (1992) 101-108.
- [3] AARNIO, P. A., ROUTTI, J. T., SANDBERG, J. V., J. Radioanal. Nucl. Chem., Articles **124** 2 (1988) 457-466.
- [4] MOENS, L., DE DONDER, J., XILEI, LIN, DE CORTE, F., DE WISPELAERE, A., SIMONITS, A., HOSTE, J., Nucl. Instr. Methods **187** (1981) 451-472.
- [5] MOENS, L., ROOS, P., J. Radioanal. Nucl. Chem., Articles **160** 1 (1992) 269-275.
- [6] DE CORTE, F., SIMONITS, A., J. Radioanal. Nucl. Chem., Articles **133** 1 (1989) 43-130.
- [7] DE CORTE, F., SIMONITS, A., DE WISPELAERE, A., J. Radioanal. Nucl. Chem., Articles **133** (1989) 131-151.
- [8] DE CORTE, F., SIMONITS, A., BELLEMANS, F., FREITAS, M. C., JOVANOVIĆ, S., SMODIŠ, B., ERDTMANN, G., PETRI, H., DE WISPELAERE, A., J. Radioanal. Nucl. Chem., Articles **169** (1993) 125-158.
- [9] SMODIŠ, B., DE CORTE, F., DE WISPELAERE, A., J. Radioanal. Nucl. Chem., Letters **186** (1994) 183-188.

- [10] DE CORTE, F., "The k_0 -Standardization Method a Move to the Optimization of Neutron Activation Analysis", Agregree Thesis, University of Ghent, Belgium, 1987.
- [11] GLADNEY, E. S., O'MALLEY, B. T., ROELANDTS, I., GILLS, T. E., NBS Special Publication 260-111, US Department of Commerce, Washington D.C. (1987).
- [12] STROPNIK, B., BYRNE, A.R., SMODIŠ, B., Acta Chim. Slovenica **40** (1993) 301-330.
- [13] STROPNIK, B., BYRNE, A.R., SMODIŠ, B., JAČIMOVIĆ, R., Acta Chim. Slovenica **41** (1994) 65-82.
- [14] SVETINA GROS, M., SMODIŠ, B., PIRC, S., Acta Chim. Slovenica **40** (1993) 243-253.
- [15] SMODIŠ, B., STROPNIK, B., Analyst, **119** (1994) 2061-2065.
- [16] SVETINA, M., SMODIŠ, B., JERAN, Z., JAČIMOVIĆ, R., J. Radioanl. Nucl. Chem., Articles **204** (1996) 45-55.
- [17] KAYZERO/SOLCOI for reactor-neutron activation analysis (NAA) using the k_0 standardization method, DSM Research, Geleen, Netherlands.
- [18] SMODIŠ, B., JAČIMOVIĆ, R., JOVANOVIĆ, S., STEGNAR, P., VUKOTIĆ, P., Vestn. Slov. Kem. Drus. **35** (1988) 397-408.
- [19] STEGNAR, P., STROPNIK, B., KRIŽMAN, M., MLJAČ, L., KOBAL, A.B., REBERNIK, J., DEJANOVIĆ, B., Report the ecological burden at working places in the Šoštanj Thermal Power Plant, and an evaluation of the health and working capacity of the workers, Ljubljana, (1993) (in Slovene).
- [20] KUMP, P., NEČEMER, M., ŠNAJDR, J., Spectrochimica Acta Part B **51** (1996) 499-507.
- [21] INJUK, J., Van GRIEKEN, R., KLOCKENKÄMPER, R., Von BOHLEN, A., KUMP, P., Spectrochimica Acta Part B **52** (1997) 977-984.
- [22] Van ESPEN, P., JANSSENS, K., NOBELS, J., Chemom. Intell. Lab. Syst., **1** (1986) 109.
- [23] Yugoslav standard for obligatory use from 1.1.1970: Protection at Work - Maximum allowable concentration of harmful gases, vapors and aerosols in the atmosphere of working areas. JUS Z.BO.001. Službeni list SFRJ br. 35/1971 (in Serbo-Croatian).
- [24] Air quality guidelines for Europe, (1987) WHO regional publications, European series; No. 23, ISBN 92-890-1114-9, WHO, Copenhagen.