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ESRF

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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** *Quantitative measurement of the micro-heterogeneity of certified reference materials: method development and application*	**Experiment number**: CH-1001
Beamline: ID18F	**Date of experiment**: from: July 2000 to: June 2002	**Date of report**: 26/02/2003
Shifts: 120	**Local contact(s)**: Dr. Andrea SOMOGYI Dr. Michael DRAKOPOULOS	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Final Report of the Long Term Project CH1001 at ESRF ID18F:

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1. General description of the project

1.1. Background of the project

A collaboration agreement for a period of 3 years was signed in 1999 between the ESRF and the Micro & Trace Analysis Centre (MiTAC) of the University of Antwerp. The collaboration was described as: "*A micro-XRF instrument shall be installed in the ESRF at the ID18 beamline maintained in a configuration so as to provide stable working conditions for sensitive and accurate quantitative chemical analysis to be used for the determination of trace constituents and the sensitive and accurate chemical analysis on the microscopic level, including mapping and X-ray tomography. There are many application areas of growing importance…. In addition there are many advantages of such a system in metrology as a validation tool of other microscopic analytical techniques"*. In the collaboration agreement the partners also expressed the intention to collaborate in the Fifth EU Framework Programme in the area of metrology ("Competitive Growth") for work in accurate elemental analysis with the ID18F beamline.

The MiTAC participated in the construction and testing of ID18F in collaboration with ID22. Our group contributed to the acquisition of hardware for the beamline through the delivery of instrumentation with an acquisition value of ca. 150 Keuro which included focusing optics (CRL), spectrometer table and motor stages, CCD camera and optical microscope for sample alignment, analog detector electronics and a Si(Li) detector. One member of MiTAC personnel (Dr. Andrea Somogyi) is stationed full time at the ESRF from September 1999 for assistance in construction, testing and exploitation of the instrument. The ID18F instrument was commissioned in September 2001.

An EU RTD project (duration 3 years) became effective in January 2001: "*Synchrotron Microanalysis: accurate and traceable elemental analysis on the microscopic level, MICRO-XRF*". The project coordinator is MiTAC, the ID22 group is a partner together with 4 other European partners. Work packages concern the optimization/use of ID18F as a quantitative tool for elemental microanalysis with the potential for validation of other beam methods and the elaboration of certified/standard reference materials.

The obligations of ID22 and MiTAC in the MICRO-XRF EU project and the collaboration agreement were covered from July 2000 to June 2002 in the present ongoing long term project at ID18F.

1.2. Aims of this project

The analytical development work of this long-term project contributes to a significant expansion of ESRF capacity for quantitative elemental analysis on the microscopic level, both for outside users and for in-house use. It also leads to a better understanding of and control over the aspects of accuracy and precision of the analytical methodology in trace element microanalysis. The experimental sessions of the project included the study of microfocusing optics, beam stability and linear polarisation, the optimisation of the instrument in terms of detection limits, tests of analog and digital detector electronics, different types of solid-state detectors and various optical elements. The latter included the tests of several CRLs and OSMIC bent multilayer optics. As determined in these experiments, aiming at the analytical characterization of the ID18F spectrometer, detection limits down to the 10 ppb level is achieved for the most efficiently excited transition metals in light element matrices with a typical beamsize of 15(H) x 2(V) μm^2.

Applications of the ID18F instrument included a number of studies investigating the micro-heterogeneity properties of certified reference materials (CRMs), NIST standard reference materials (SRMs) and geological standard glasses for microscopic analysis. The work involved:

- the contribution to the finalization of the construction of a highly stable micro-SRXRF end station (ID18F) together with ESRF staff;
- the extension of the lateral resolution to (H×V) 15×2 micrometer;
- the extension of the detectable analyte concentration levels down to the sub-ppm level (i.e., analyte mass less than 1.0 fg) and the accuracy of analytical data to 5%;
- the determination of the heterogeneity of a number of available CRMs, SRMs and reference materials and their stability in time.

2. Long term project, general aspects of experimental sessions

The period of the long term project extends from July 2000 to June 2002. In this period 120 shifts were repartitioned over 7 experimental sessions. The study of the analytical characteristics of the ID18F beamline started with a preliminary experimental session in April 2000 (15 shifts) that will also be briefly reviewed in this report.

3. Experimental sessions

3.0. Experimental session 0 (17-21 April 2000, 15 shifts, prior to start of long term project)

Participants: M. Drakopoulos, A. Somogyi, B. Vekemans, L. Vincze
Topics: test of detector and detector electronics

- determination of the intensity, spot-size, divergence and degree of polarization of the focused beam;
- stability measurements, effect of change of the heat-load on the monochromator crystal (due to SR ring refill), misalignment of the lens, comparison of the ionization chamber (OKEN) and photo-diode (Eurysis) detectors;
- characterization of different types of solid-state detectors (Gresham Si(Li) detector and PGT HPGe detector from the ESRF detector pool, CANBERRA HPGe detector with amplifier for high count rate measurements from MiTAC).
- determination of the detection limits in different geometrical conditions (different sample-detector distance and detector collimators) using different standards and detectors

Based on these measurements the Antwerp group acquired instrumentation for the ID18F beamline which is now available for the beamline (sample-table and stages, analog detector electronics, Si(Li) detector). The employed quantification approach includes a sophisticated **spectral deconvolution algorithm** (LINUX-AXIL) coupled with a "no-compromise" solution for the quantification problem based on a well-established **Monte Carlo simulation code** for photon-matter interactions both developed in the MiTAC laboratory. For the focusing optics 2 approaches were selected for further evaluation, CRL lenses and bent multilayer optics (OSMIC MAX-FLUXTM).

3.1. Experimental session 1 (26 October-6 November 2000, 30 shifts)

Participants: M. Drakopoulos, L. Kempenaers, A. Somogyi, B. Vekemans, L. Vincze
Topics: with CRL @ 21 keV: measurements on NIST SRM 1577 Bovine Liver, NIST SRM 613 Trace elements in glass, NIST SRM 1573a Tomato Leaves, BCR CRM 680 PolyEthylene (PERM T3), NIST SRM 1570a Spinach Leaves; with CRL @ 27 keV: BCR CRM 680 PolyEthylene (PERM T3), Allende 1 (Q-Phase). Study of stability of the beam with micro-ionisation chamber.

- To investigate the micro homogeneity of the reference materials each were measured as follows:

(i) repetitive point measurement on the same point (100 points, 50 sec per point)
(ii) mapping 21 × 21 points (step size equal to beam size, 50 sec per pixel)
(iii) mapping 21 × 21 points (step size equal to 100 micrometer, 50 sec per pixel)
These measurements were performed with the Gresham Si(Li) detector from the ESRF detector pool together with the ID18F analog detector electronics.

These measurements were performed using a Gresham Si(Li) detector in conjunction with analog detector electronics of the ESRF detector pool. During the beam time, the spectrum deconvolution software LINUX AXIL on the remote PC brick11 was evaluated. The current version of the software enabled on-line spectrum evaluation during the actual experimental session.
The measurements of the Allende sample demonstrated the need of digital electronics in order to handle high fluorescent count-rates. With the analog electronics, the information of low intensity lines near dominant lines (e.g. Zn in the presence of Fe in the Allende sample) is lost due to pile-up of the dominant peaks. Reducing the intensity of the primary beam would result in increased measuring time.

A number of measurements concerned the time dependence of the X-ray intensity and harmonic contribution in the beam spot and the correction of variations through the use of a micro-ionisation chamber developed and tested for ID18F during in-house research.

3.2. Experimental session 2 (26-29 April 2001, 12 shifts)

Participants: M. Drakopoulos, A. Somogyi, B. Vekemans, L. Vincze

Topics: Osmic mirror test @ 14.4 keV, measurements of MPI-DING standards with CRL 21 keV (T1G 110 μm [analog], T1G 110 μm [DSP], ATHO-G 110 μm [DSP], St-Ho 6/80G 110 μm [DSP], BM90/21-G 110 μm [DSP]), bronze sample BEY 97 (CRL 21 keV) and bronze standards (2-7-54, 3-2-24, 4-1-41, 5-9-2); experiments to characterise the bremsstrahlung background with CRL lenses on Si, Ti, Al, Pd.

- The ID18F set-up was tested with the final components: detectors, motors, alignment camera and optics.
- The CANBERRA DSP9660 was successfully used in combination with the Gresham Si(Li) detector, resulting in faster data acquisition and spectral data of better quality.
- The performance of a confocal MAX-FluxTM optic from OSMIC (bent multilayer optics) was tested at the ID18F beam line at 14.4 keV. This characterization involves beam size (H×V) determination as a function of the distance from the optic, sensitivity to misalignment, beam intensity determination, derivation of absolute and relative detection limits including elemental yields, determination of the degree of linear polarization.
- MPI-DING Geological Reference (silicate) glasses were prepared by directly fusing and stirring 50-100 g each of basalt, andesite, komatite, peridotite, rhyolite and quartz-diorite. Purpose is to provide reference materials for geochemical *in-situ* microanalytical work, which are homogeneous with respect to major, minor and trace elements on the micrometer scale. The same type of samples was analysed by various techniques in a laboratory intercomparison study, including micro-XRF at HASYLAB. The procedure as described for the experimental session 1 was applied to study the microscopic homogeneity of these materials.

3.3. Experimental session 3 (6-12 June 2001, 18 shifts)

Participants: M. Drakopoulos, L. Kempenaers, A. Somogyi, B. Vekemans, L. Vincze
Topics: Further test of Osmic mirror, measurements of NIST SRM 1577a Bovine Liver 100 μm (CRL @ 21 keV) with different beam sizes (3.64 × 9.2 μm^2, 18 × 20 μm^2,43 × 44 μm^2, 90 × 96 μm^2), MPI-DING reference materials (CRL @ 21 keV, 3.64×9.2 μm^2) [St-Ho 6/80G 110 μm, BM90/21-G 110 μm, BCR-2G 100 μm, ML3B-G 110 μm, KL2-G 110 μm]

- The series of MPI-DING Geological Reference (silicate) glasses were measured as a continuation of the previous measuring time. Also, the NIST SRM 1577a Bovine Liver was measured with different beam sizes. These results have been published in references 5 and 8.
- The first version of a programme "microxrf1.pro" for on-line data evaluation was installed and tested during this beam time on ID18F (id18fpc1). It allows on-line spectrum evaluation (LINUX AXIL) during measurements, i.e., line and image scans on basis of the extracted elemental line intensities can be monitored as opposed to the usual post-processing of the data after the beam time session.
- The performance of the confocal MAX-FluxTM optic from OSMIC (bent multilayer optics) was tested with an incident energy around 14.4 keV. The final conclusion of the measurements was that this system did not meet the resolution requirements. Therefore it was decided to acquire a set of 200 aluminium CRL lenses from the University of Aachen. 100 of these were made available for the experimental session 4 where they could be compared with a set of lenses of ID22.

3.4. Experimental session 4 (15-20 November 2001, 15 shifts)

Participants: R. Simon, A. Somogyi, B. Vekemans, L. Vincze
Topics: Study of Raman scattering as a background contribution source on different pure metal foils, tests of the CRL lenses.

- Study of the contribution of photo/Auger electron bremsstrahlung and X-ray Resonant Raman Scattering (XRRS) to the measured XRF spectral background. The ability to quantitatively estimate their spectral contributions is required in case of standardless quantitative analysis. Moreover, these effects in many practical situations determine the achievable detection limits for a given SRXRF spectrometer installed at a 3rd generation SR source. XRF spectra of high-purity (typically better than 99.9 %) single element metal foils (*Goodfellow Ltd, UK)* were collected at specific incident energies. Measurements were done at high counting rate conditions on Cu 0.050 mm, Zn 0.250 mm, Zr 0.050 mm, Nb 0.1 mm, Mo 0.1 mm, Pd 0.025 mm, Ag 0.05 mm, In 0.1 mm, Sn 0.05 mm. The measured spectral distributions will be used to validate our new version of the MC simulation code modeling the above effects. A manuscript is in preparation.

- From the set of 100 aluminium CRL lenses delivered by the University of Aachen, a 56-element CRL lens (lens 2) was tested and compared with an available CRL lens system (lens 1) which is regularly used at ID22 because of its excellent characteristics. The experimental tests showed that the new lens 2 results in a microbeam with an optimal size comparable to the optimal beam size for lens 1 (typically [H×V] 13×1.5 μm^2), but the intensity is 34% (17keV) to 40% (14keV) lower than the intensity of the microbeam produced by lens 1.
- The IDL microxrf2.pro code (version November 2001) was installed and tested on the evaluation-PC at ESRF ID18F (id18fpc1) during this beam time session. The microxrf2.pro code includes the XRF quantification by means of an inverse Monte Carlo simulation code. It was used for the measurement of the beam stability of ID18F. Results were discussed at the 2001 Denver X-ray Conference in August 2001 and presented at the SRMS-3 Singapore conference in January 2002.

3.5. Experimental session 5 (31 January – 5 February 2002, 15 shifts)

Participants: M. Drakopoulos, A. Somogyi, S. Tougaard (University of Southern Denmark), B. Vekemans, L. Vincze
Topics: measurement of 12 samples of ZnO thin-films, NIST SRM 1570a Spinach, NIST SRM 1573a Tomato Leaves, BCR CRM 680 PolyEthylene (PERM T3)

- 12 samples of ZnO thin-films were produced in the spring of 2001 and were measured using CRL @ 14.4 keV at 1.5×12.7 μm^2). These thin films were previously studied by means of angle resolved-XPS and XPS-peak shape analysis. Additionally, PIXE, RBS (University of Oxford) and XRF measurements (ANKA Fluo beam line) are planned to take place during the coming months in the framework of the Micro-XRF EU project. The purpose of these measurements was to compare the results of the different techniques for determination of the amount of substance at surfaces and thus to validate results obtained with ID18F. Four depositions of ZnO were measured (1.6, 3.8, 6.8 and 10.7×10^{15} Zn at./cm^2) on 3 substrates (100 nm SiO_2 thermally grown on Si (100), Al previously bombarded with 3 keV O^{2+} ions, 1 mm thick Al_2O_3).
- Measurements on several reference materials were performed (CRL @ 21 keV, 20×25 μm^2) as continuation of the investigation on the micro homogeneity of these materials in the experimental session 1.
- The detailed Monte Carlo simulation code, version msim5d, was adapted for use in parallel-computing mode (SMP). For this, an overlaying code called "mcs_smp" was developed to distribute the MC simulation tasks evenly over individual CPUs when required. The calculation time of complicated simulation tasks can thus be significantly reduced, in principle by a factor nearly equal to the number of CPUs available.
  The microxrf2.pro code (version January 2002) includes the possibility of using the SMP capabilities of the system. This version also includes principal component analysis and K-means clustering of the image pixels (intensity or concentration values). During this beam time the microxrf2.pro code has been made available also to users of ID22 and ID21 by installation of the software on the evaluation PC configurations of the beam lines ID22 and ID21.
- The accuracy of the Monte Carlo simulation was tested against experimental spectra of several SRMs. Accuracies were achieved in the 2-4% range for thin glass and 1-12% for geological materials, see reference 4.

3.6. Experimental session 6 (29 April-6 May 2002, 18 shifts)

Participants: M. Drakopoulos, A. Somogyi, B. Vekemans, L. Vincze, U. Wätjen
Topic: Measurement of heterogeneity of certified reference material of IRMM, trace elements in sediment.

IRMM BCR samples were prepared by directly pressing pellets of appropriate thickness (250-500 micron):

- BCR-176R incineration ash; particle size < 105 micron; elements (indicative concentrations in ppm): As (55) Cd (200) Co (25) Cr (700) Cu (1000) Fe (13000) Hg (1.5) Mn (700) Ni (100) Pb (4800) Sb (830) Se (20) Tl (1.5) V (30) Zn (16000).
- BCR-277R estuarine sediment; particle size < 125 micron; elements (indicative concentrations in ppm): As (20) Cd (0.6) Co (20) Cr (200) Cu (70) Fe (50000) Pb (35) Sb (1) Zn (200).
- BCR-280R lake sediment; particle size < 150 micron; elements (indicative concentrations in ppm): As (30) Cd (0.8) Co (20) Cr (100) Cu (60) Fe (40000) Pb (130) Sb (1) Th (10) Zn (200).

- BCR-320R canal sediment; particle size < 90 micron; elements (indicative concentrations in ppm): As (20) Cd (3) Co (10) Cr (60) Cu (50) Fe (27000) Pb (90) Sb (2) Th (5) Zn (300).

Combined repetitive scans of the same spot and image scans on the pellets with a 4.1 µm (V) × 15 µm (H) 28 keV X-ray beam were performed in order to investigate the elemental distribution in the pellets and to determine the minimum sampling masses for the trace-elements present in these standards.

3.7. Experimental session 7 (4-8 June 2002, 12 shifts)

Participants: M. Drakopoulos, K. Proost, B. Vekemans, J. Osan
Topic: Influence of artificial aging of trace element loaded polymer certified reference material.

IRMM BCRs VDA 001 and CRM 680 (PERM T3) were subjected to a 56 day UV treatment in order to accelerate the aging of the plastics. Combined repetitive scans of the same spot and image scans were performed at 21 keV and 27 keV with different beam sizes varying from 1.6 µm (V) × 4 µm (H) up to 99 µm (V) × 96 µm (H) in order to investigate the influence of aging and UV-stability of polymer CRMs. Accelerated aging by exposure of materials by UV-light offers a practical means of investigating the durability of the matrix and the stability of the elemental composition of a reference material. It is important that the physical and chemical changes induced by artificial aging duplicate those resulting from natural aging under standard laboratory conditions. The correlation between the time scales of accelerated and natural aging in case of the BCR CRM 680 is not experimentally known in literature and precise predictive theoretical models are not available. Therefore, some assumptions have to be made to transform the time scale of UV-induced accelerated aging experiments to aging under laboratory conditions (20 °C).
Upon exposure to UV-photons that interact with the PE-matrix, heat is built up in the material. Furthermore, chemical degradation of the polymer takes place as a result of photo-chemical induced processes, such as chain-scission and cross-linking, accompanied by formation of carbonyl, carboxyl, hydroxyl functional groups and of peroxides. It is believed that the rate of physico-chemical changes increases with a factor of 15 with respect to laboratory conditions. An exposure time of 60 days of accelerated aging therefore corresponds to an exposure time of 900 days (2½ years) at normal laboratory conditions.

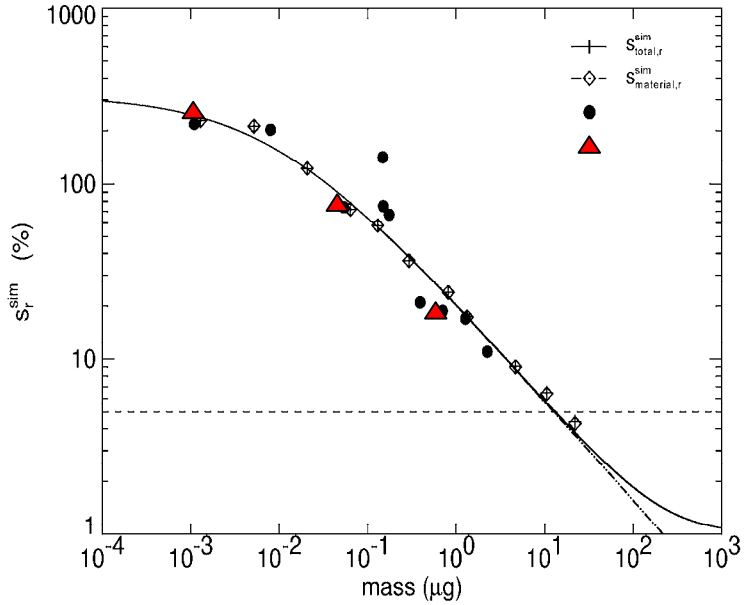

Fig. 1. $s^{sim}_{total,r}$ **and** $s^{sim}_{material,r}$ **values vs. analyzed mass *m* of Cr in the BCR CRM 680 sample model obtained with** S_{island} **= 10 × 10 µm². The corresponding** $s^{exp}_{material,r}$ **values for Cr of both samples (original and UV) are also indicated.**

To investigate any difference in heterogeneity between a sample subjected to UV-light and its original status, the procedure for calculating $m_{min,5\%}$ was applied for BCR CRM 680 in the same way as described in section 3.1., and by analyzing the sample using three different sampling masses: 1.1, 54 and 701 ng. These values for Cr(UV) in BCR CRM 680 are plotted in Fig. 1 on top of the (Cr, original) values from the original sample.

From Fig.1, we observe that the (Cr, UV) values are slightly lower than the (Cr, original) values. However, the difference between the two values is situated within the uncertainty interval of the estimated mmin,5% values. For the other trace elements in the polymer sample, the same non-significant difference between the (original) and (UV) values were observed. From Fig.1, we conclude that the trace elements in BCR CRM 680 material are UV-light resistant and that the concentration values and the homogeneity of the polymer material will not be affected even after a period of more than two year storage in typical laboratory conditions (see also Ref.12).

5. General conclusions

In general, the design goals put forward for ID18F were met for point and 2D analysis (5% accuracy, spatial resolution down to [H×V] 15×2 micrometer*)*. The degree of linear polarization of the beam was assessed in various measurement conditions. It was estimated to be better than 98-99%. As the degree of polarization could change with time, further measurements will be needed to estimate the overall degree of linear polarization. Sensitive analysis is possible with detection limits of 2-4 fg absolute mass for Ca down to 0.2 fg for Cu in 1000 sec. On the basis of the iterative Monte Carlo method used the accuracy of analysis is nearly consistent with the accuracy of the employed physical constants. A number of secondary interaction processes of X-rays with the sample and the detector were studied in order to improve the accuracy on the determination of trace elements (photoelectron Bremsstrahlung and resonant Raman interaction). These are now being adopted in the MC simulation code.

The stability of the ID18F spectrometer was regularly tested during the different experimental sessions. It is demonstrated that the miniature ionization chamber (ESRF in-house development) monitors adequately the analyzing microbeam.

An attempt to use confocal MAX-FluxTM optic from OSMIC (bent multilayer optics) as a focusing device failed because the company could not deliver a device with the required beam size specifications. A set of 200 parabolic compound refractive lenses (CRL) in Al was then selected as the focusing optics in the system. Selected fixed sets of these lenses can be assembled to cover the entire available energy range of 6-28 keV. The first tests of the delivered lenses have shown that a 2 micrometer vertical spot-size is available but that the transmission is considerably smaller than expected. The losses in flux loss were temporarily compensated by the increased available flux of the undulators**.** Their replacement by improved CRL with better transmission occurred during the first half of 2002.

A number of reference materials were studied in detail. The values of the minimum representative mass that can be measured with 5 % reproduciblity ($m_{min,5\%}$) of different elements are determined for NIST and USGS reference materials were measured. We can conclude that in order to employ these USGS and NIST reference materials, at least 60 ng of the material must be employed. When Cu and Zn are omitted the minimal representative mass drops to ca. 20 ng for all the seven glass materials. These results are published in papers in Anal.Chem and the Journal of Analytical Atomic Spectrometry (JAAS). The evaluation of the USGS geological reference (silicate) glasses (experimental data from the experimental sessions 2 and 3) is published. Next to the homogeneity/heterogeneity study, these results are useful for the verification and validation of the quantification scheme based on the iterative use of the MC simulation code for XRF spectroscopy**.**

5. Publications and conference presentations.

5.1. Publications

1. A. Somogyi, M. Drakopoulos, L. Vincze, B. Vekemans, C. Camerani, K. Janssens, A. Snigirev and F. Adams, *ID18F: a new micro-x-ray fluorescence end-station at the European Synchrotron Radiation Facility (ESRF): preliminary results*; X-Ray Spectrometry, 30: 242-252 (2001).
   Abstract. A new user end-station is under construction at the ESRF with collaboration between the Micro-Fluorescence, Imaging and Diffraction beamline (ID22) and the Micro and Trace Analysis Center (MiTAC) of the University of Antwerp. The new end-station is dedicated to quantitative micro-fluorescence measurements. The analytical characteristics (degree of polarization of the incoming beam, absolute and relative detection limits) of the new set-up were investigated during the preliminary experiments by using a temporary experimental set-up.

2. F. Adams, *SR Micro X-ray Fluorescence Analysis, a Tool to Increase Accuracy in Microscopic Analysis*; Nuclear Instruments and Methods B 199 (2003) 375-381.
Abstract. Microscopic X-ray fluorescence analysis has potential for development as a certification method and as a calibration tool for other microanalytical techniques. The interaction of X-rays with matter is well understood and modelling studies show excellent agreement between experimental data and calculations using Monte Carlo simulation. The method can be used for a direct iterative calculation of concentrations using available high accuracy physical constants. Average accuracy is in the range of 3-5 % for micron sized objects at concentration levels of less than 1 ppm with focused radiation from SR sources. The end-station ID18F of the ESRF is dedicated to accurate quantitative micro-XRF analysis including fast 2D scanning with collection of full X-ray spectra. Important aspects of the beamline are the precise monitoring of the intensity of the polarized, variable energy beam and the high reproducibility of the set-up measurement geometry, instrumental parameters and long-term stability.
3. A. Somogyi, M. Drakopoulos, L. Vincze, B. Vekemans, M. Kocsis, A. Simionovici and F. Adams, *Effects of Beamline Components (Undulator, Monochromator, Focusing Device) on Beam Intensity of ID18F Microprobe End-station (ESRF)*; Nuclear Instruments and Methods B 199 (2003) 559-564.
Abstract. The ID18F microprobe end-station of the European Synchrotron Radiation Facility (ESRF) is dedicated to precise and reproducible quantitative X-ray fluorescence analysis in the ppm level with ≤5 % accuracy for elements of Z≥19 and micron-size spatial resolution. In order to fulfill this requirement the precise monitoring and normalization of the intensity variation of the focused micro-beam is necessary. The various effects influencing the intensity variation, hence the stability of the μ-beam, were investigated by placing different detectors (miniature ionization chamber, photodiodes) into the monochromatic beam. The theoretical statistical error of the measured signal in each detector was estimated on the basis of the absorption and e^--ion-pair production processes and was compared with the measured statistical errors.
4. B. Vekemans, L. Vincze, A. Somogyi, M. Drakopoulos, L. Kempenaers, A. Simionovici and F. Adams, *Quantitative X-ray Fluorescence Analysis at the ESRF ID18F Microprobe*; Nuclear Instruments and Methods B 199 (2003) 396-401.
Abstract. The new ID18F end-station at the ESRF (European Synchrotron Radiation Facility) in Grenoble (France) is dedicated to sensitive and accurate quantitative micro X-ray fluorescence (XRF) analysis at the ppm level with accuracy better than 10% for elements with atomic numbers above 18.
For accurate quantitative analysis, given a high level of instrumental stability, major steps are the extraction and conversion of experimental X-ray line intensities into elemental concentrations. For this purpose a two-step quantification approach was adopted. In the first step, the collected XRF spectra are deconvoluted on the basis of a non-linear least-squares fitting algorithm (AXIL). The extracted characteristic line intensities are then used as input for a detailed Monte Carlo (MC) simulation code dedicated to XRF spectroscopy taking into account specific experimental conditions (excitation/detection) as well as sample characteristics (absorption and enhancement effects, sample topology, heterogeneity etc.). The iterative use of the MC code gives a 'no-compromise' solution for the quantification problem.
5. Kempenaers L, Janssens K, Vincze L, et al. *A Monte Carlo model for studying the microheterogeneity of trace elements in reference materials by means of synchrotron microscopic X-ray fluorescence* Anal.Chem.74: (19) 5017-5026 (2002).
Abstract. Syncrotron micro-XRF, a trace level microanalytical lethod, allows quantitiative study of the nature and degree of heterogeneity of inorganic trace constituents in solid materials with homogeneoues matirx. In this work, the standard reference materials NIST SRM 613, Trace Elements in 1 mm Glass wafers, and NIST SRM 1577a Trace Elements in Bovine Liver, are examined at the 10-100 ng mass level using X-ray beams of 5-150 μm in diameter. A procedure based on a large number of repeated analyses of small absolute amounts of SRMs allows calculation of the minimal representative mass of the standard. A Monte Carlo simulation model was constructed for both homogeneous and heterogeneous materials to elucidate the dependence of the calculated minimal representative mass on the total analysed mass in the case of materials that show strongly heterogeneous features at the microscopic level.
6. Jochum K.P., …, Janssens K., …, Vincze L., …, Zimmer M., *The preparation and preliminary characterization of eight geological MPI-DING reference glasses for in-situ microanalysis*; Geostandards Newsletter, Vol.24.1, (2000), 87-113.

Abstract. Eight silicate glasses were prepared by directly fusing and stirring 50-100 g each of basalt, andesite, komatiite, peridotite, rhyolite, and quartz-diorite. These are referred to as MPI-DING glasses and were made for the purpose of providing reference materials for geochemical, in-situ microanalytical work. Results from various analytical techniques indicate that individual glass fragments are well homogenised with respect to major and trace elements at the μm to mm scale. Heterogeneities due to quench crystallisation of olivine have been observed in small and limited areas of the two komatiitic glasses. In order to obtain concentration values for as many elements as possible, the glasses were analysed by a variety of bulk and microanalytical methods in a number of laboratories. From the analytical data, preliminary reference values for more than sixty elements were calculated. The analytical uncertainties of most elements are estimated to be between 1% and 10%.

7. Vincze L., Somogyi A., Osán J., Vekemans B., Török S., Janssens K. and Adams F. *Quantitative trace element analysis of individual fly-ash particles by means of microscopic X-ray fluorescence* Anal.Chem. (2002) 74 1128-1135.
   A new quantification procedure was developed for the evaluation of micro X-ray fluorescence (XRF) data-sets obtained from individual particles, based on iterative Monte Carlo (MC) simulation. Combined with the high sensitivity of synchrotron radiation induced XRF spectroscopy, the method was used to obtain quantitative information down to trace-level concentrations from micron-sized particulate matter. The detailed XRF simulation model was validated by comparison of calculated and experimental XRF spectra obtained for glass microsphere standards, resulting in uncertainties in the range of 3-10 % for the calculated elemental sensitivities. The simulation model was applied for the quantitative analysis of X-ray tube and synchrotron radiation induced scanning micro-XRF spectra of individual coal and wood fly ash particles originating from different Hungarian power plants. By measuring the same particles by both methods the major, minor and trace-element composition of the particles were determined. The uncertainty of the MC based quantitative analysis scheme is estimated to be in the range of 5-30 %.
8. L. Kempenaers, K. Janssens, K. P. Jochum, L. Vincze, B. Vekemans, A. Somogyi, M. Drakopoulos, A. Simionovici and F. Adams, *Micro-heterogeneity study of trace elements in USGS and NIST glass reference materials by means of synchrotron micro-XRF*; accepted in J. Anal. At. Spectrom. (2002).
   Abstract. Synchrotron μ-XRF (X-ray fluorescence analysis), a trace level micro analytical method, allows to quantitatively study the nature and degree of heterogeneity of inorganic trace constituents in a number of reference materials with a homogeneous matrix. In the present study, glass materials of NIST and USGS containing trace levels of heavy metals are concerned. The measurements involve an extensive series of local analyses, performed in identical conditions at different locations on the material.
   In this paper, the procedure is employed to measure the degree of micro-heterogeneity of several existing reference materials from NIST and USGS and to evaluate their suitability for calibration of trace-level micro-analytical methods. After analyzing the micro-heterogeneity of trace elements in these reference materials, a minimum representative mass for homogeneous measurements is calculated.
9. *ID18F: a new X-ray microprobe end-station*. Submitted (November 2001) for publication in ESRF Highlights.
   Introductory paragraphs. A new user end-station, ID18F, dedicated for precise and reproducible X-ray microprobe measurements, is constructed in the 3rd experimental hutch of the ID18F beam-line of the ESRF in collaboration between the ID22 beam-line and the MiTAC laboratory of the University of Antwerp, Belgium. The activities are also funded through the EU Project (Growth Programme), Micro-XRF. The goal of the end-station is to improve procedures of micro-X-ray fluorescence analysis in order to reach 5-10 % average accuracy of quantification down to sub-ppm concentration levels for elements of $Z>13$. In order to achieve this goal high reproducibility of the measurement geometry and instrumental parameters of the set-up, very good short and long-term stability and precise monitoring (<1%) of the intensity variation of the incoming beam are required.
10. M. Kocsis, A. Somogyi, *Miniature ionization chamber detector developed for X-ray microprobe measurements*; Accepted in J. Synch. Radiation (2001).
    Abstract. A windowless small ionization chamber detector was developed for monitoring the intensity of the micro-beam at the ID18F micro-probe end-station of the European Synchrotron Radiation Facility. The small dimensions of the ionization chamber (10 mm along the beam direction and 5 mm perpendicular to it) make it possible to place it very close to the sample. A pinhole of 50 mm diameter was used for defining the entrance window of the ionization chamber thus the small counter can be used as an order selecting aperture while measuring simultaneously the intensity after the aperture. In the

present work the technical characteristics, such as current-voltage curve, stability and linearity of the small monitor were tested.

11. Vincze, L. Janssens, K., Vekemans B., Adams F.,
Monte Carlo simulation for X-ray fluorescence spectroscopy (book chapter),
In: X-Ray Spectrometry Based on Recent Technological Advances, Ed. Kouichi Tsuji, Jasna Injuk and R. Van Grieken, [edit.], Publisher: John Wiley & Sons, Ltd. (in druk) (2003).
12. L. Kempenaers, *Micro heterogeneity study of trace elements in reference materials* Ph.D. Thesis University of Antwerp (submitted for defense, 2003).

5.2. Conferences and meetings

European Conference on Energy-dispersive X-ray Spectrometry, Krakow, Poland (18-23 June 2000)

- *Modeling of X-ray Fluorescence and Scattering Experiments*; L. Vincze, K. Janssens, B. Vekemans, F. Adams. Invited lecture.
- *ID18F: A new X-ray microprobe end-station at the European Synchrotron Radiation Facility;* M. Drakopoulos, A. Somogyi, L. Vincze, B. Vekemans, K. Janssens, A. Snigirev, F. Adams. Oral presentation.
- *ID18F: A new X-ray microprobe end-station at the European Synchrotron Radiation Facility (ESRF), preliminary results*; A. Somogyi, M. Drakopoulos, L. Vincze, B. Vekemans, K. Janssens, A. Snigirev, F. Adams. Poster presentation. *Poster award*.

Eleventh ESRF Users' Meeting (19 February 2001)

- Synchrotron Microanalysis: Accurate and Traceable Elemental Analysis on the Microscopic Level. Acronym: MICRO-XRF Generic Activity 2: MEASUREMENT & TESTING European Union Fifth Framework project. Poster presentation.

ANKA Prospective User Meeting (29-30 March 2001)

- *Modeling of X-ray fluorescence and absorption spectroscopy experiments;* L. Vincze, B. Vekemans, K. Janssens, A. Somogyi, M. Drakopoulos, A. Snigirev, F. Adams. Oral presentation.
- *European Micro-XRF Project. ESRF Beamline ID18F: Present Status*; B. Vekemans, A. Somogyi, M. Drakopoulos, L. Vincze, K. Janssens, A. Snigirev, and F. Adams. Oral presentation.

Aussois Science Days Seminar, Aussois, France (9-11 May 2001)

- ID18F: NEW MICRO-X-RAY FLUORESCENCE END-STATION AT THE ESRF, A. Somogyi, M. Drakopoulos, L. Vincze, B. Vekemans, K. Janssens, A. Snigirev , A. Simionovici and F. Adams. Poster presentation.

International Congress on X-ray Optics and Microanalysis (ICXOM-XVI), Vienna, Austria (2-6 July 2001)

- *A New endstation for X-ray microprobe analysis at the ESRF: ID18F*; M. Drakopoulos, A. Snigirev, A. Somogyi, L. Vincze, B. Vekemans, L. Kempenaers, F. Adams. Oral presentation
- *Monte Carlo simulation for X-ray fluorescence and absorption spectrometry*; L. Vincze, K. Janssens, B. Vekemans, K. Proost, A. Somogyi, F. Adams, M. Drakopoulos, A. Snigirev. Oral presentation
- *The micro-heterogeneity characterization of heavy metals in low-Z reference materials by means of synchrotron micro-XRF*; L. Kempenaers, L. Vincze, B. Vekemans, K. Janssens, F. Adams, M. Drakopoulos, A. Somogyi, A. Snigirev. Oral presentation.

XXXII Colloquium Spectroscopicum Internationale (XXXII CSI), Pretoria, South Africa (8-13 July 2001)

- *ID18F, a New End-station at the ESRF for Quantitative Microscopic XRF Analysis*; F. Adams, A. Somogyi, L. Vincze, B. Vekemans, M. Drakopoulos, C. Camarani, A. Snigirev. Invited keynote lecture.

2001 Denver X-ray Conference (DXC2001), Steamboat Springs, Colorado, USA (30 July - 3 August 2001)

- *The ID18F microprobe endstation at the European Synchrotron Radiation Facility (ESRF);* A. Somogyi, M. Drakopoulos, L. Vincze, B. Vekemans, M. Kocsis, A. Snigirev and F. Adams. Poster presentation. *Poster award.*
- *Quantitative X-ray Fluorescence Analysis at the ESRF ID18F Microprobe*; B. Vekemans, L. Vincze, A. Somogyi, M. Drakopoulos, L. Kempenaers, A. Snigirev and F. Adams. Poster presentation.

SRMS-3 conference, Singapore (21-24 January 2002)

- *SR Micro X ray Fluorescence Analysis, a Tool to Increase Accuracy in Microscopic Analysis*; F. Adams. Invited lecture.
- *Effects of Beamline Components (Undulator, Monochromator, Focusing Device) on Beam Intensity of ID18F Microprobe End-station (ESRF)*; A. Somogyi, M. Drakopoulos, L. Vincze, B. Vekemans, M. Kocsis, A. Simionovici and F. Adams. Oral presentation.
- *Quantitative X-ray Fluorescence Analysis at the ESRF ID18F Microprobe*; B. Vekemans, L. Vincze, A. Somogyi, M. Drakopoulos, L. Kempenaers, A. Simionovici, and F. Adams. Oral presentation.

IRRMA-V 5th International Topical Meeting on Industrial Radiation and Radioisotope Measurement Applications, Bologna, Italy (9-14 June 2002)

- *A Monte Carlo Model for Synchrotron Radiation X-ray Fluorescence Analysis*; L. Vincze, K. Janssens, B. Vekemans, A. Somogyi, M. Drakopoulos, A. Simionovici, F. Adams.

EnviroAnalysis '2002 The Fourth International Conference on Monitoring and Measurement of the Environment, Toronto, Canada (27-31 May 2002)

- *Synchrotron radiation micro-X Ray fluorescence analysis, a tool to increase accuracy in microscopic analysis* , F. Adams, Invited keynote lecture

European Conference on Energy Dispersive X-Ray Spectrometry, Berlin (16-21 June 2002)

- *The ID18F Micro-probe End-station at the European Synchrotron Radiation Facility (ESRF)*; A. Somogyi, M. Drakopoulos, B. Vekemans, L. Vincze, K. Janssens, A. Simionovici, and F. Adams.
- *X-Ray Fluorescence Quantification at the ESRF ID18F Microprobe*; B.Vekemans, L. Vincze, A. Somogyi, M. Drakopoulos, A. Simionovici, and F. Adams.
- *A Monte Carlo Model for Studying the Micro-heterogeneity of Trace Elements in Standard Reference Materials (SRM) by means of Synchrotron Micro-XRF*; L. Kempenaers, K. Janssens, L. Vincze, B. Vekemans, A. Somogyi, M. Drakopoulos, A. Simionovici, and F. Adams.

Denver X-ray Conference, Colorado Springs, Colorado, USA (29 July – 2 August 2002)

- *Quantitative aspects of microbeam X-ray analysis,* Book of abstracts p.183*;* L. Vincze (Invited lecture).

Euroanalysis XII Conference, Dortmund, Germany (8-13 September 2002)

- *The use of synchrotron radiation in analytical chemistry at the microscopic level.* K. Janssens, invited keynote lecture.

NICKEL 2002, Sixth International Nickel Conference on Ecologic, Toxicologic and Human Health Associated with Mining, Refining and Production, Murmansk, Russia (1-6 September, 2002)

- *SR X-Ray Methods for the Characterisation of Environmental Particles*, Freddy Adams, Koen Janssens, Kristof Proost, Bart Vekemans and Laszlo Vincze, invited keynote lecture.

Hamburg workshop: applications of synchrotron radiation in chemistry- status and future (16-17 September 2002) Hamburg FRGermany.

- *SR X-ray methods for the characterisation of environmental particles*. F. Adams. Invited lecture