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Technical note

Total Re ection X-ray Fluorescence attachment module modi ed for analysis in vacuum

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abstract

Based on the design of the low cost Total Re ection X-Ray Fluorescence attachment module available since 1986 from Atominstitut (WOBRAUSCHEK-module) which can be attached to existing X-ray equipment, a new version was developed which allows the analysis of samples in vacuum. This design was in particular possible as the Peltier cooled light weight Silicon Drift Detector is following all adjustment procedures for total re ection as angle rotation and linear motion. The detector is mounted through a vacuum feed and O-ring tightening to the small vacuum chamber. The standard 30 mm round quartz, Si-wafer or Plexiglas re ectors are used to carry the samples. The re ectors are placed on the reference plane with the dried sample down looking facing in about 0.5 mm distance the up looking detector window. The re ectors are resting on 3 steel balls de ning precisely the reference plane for the adjustment procedure. As the rotation axis of the module is in the plane of the re ector surface, angle dependent experiments can be made to distinguish between lm and particulate type contamination of samples. Operating with a Mo anode at 50 kV and 40 mA with a closely attached multilayer monochromator and using a 10 mm^2 KETEK silicon drift detector with 8 m Be window, a sensitivity of 70 cps/ng for Rb was measured and detection limits of 2 pg were obtained.

1. Introduction

Total Re ection X-ray Fluorescence is a well established technique for trace element analysis specially suited for samples where small amounts are available [1–3]. Besides chemical analysis also wafer surface analysis for contamination control is a routine application for TXRF [4].There are several stand alone instruments commercially available for trace element analysis as well as for wafer surface analysis, but only one attachment module for chemical analysis using existing X-ray tube and X-ray generator — the so called WOBI module [5]. These attachment modules have been distributed to about 50 countries around the world through the Technical Cooperation program of the International Atomic Energy Agency (IAEA) and are working successfully in several developing countries allowing, with simple instrumentation, trace element analysis down to the ng/g level (equivalent to pg in the absolute units).

However, there is a lack of TXRF equipment suitable to determine light elements. Only 2 types of instruments are operating under vacuum conditions, the Rigaku Wafer analyser [6] and the WOBIS-TRAX from Atominstitut [7]. The growing demand for determination of light elements has lead to the project to adapt the WOBI-module to be operated under vacuum conditions. This new vacuum version of the TXRF module is chosen to reduce the background due to scattering in air, to avoid the Ar peak in the spectrum and to avoid the absorption of the low energy uorescence radiation emitted by low Z element atoms. The industrial development and commercial availability of small, light weight and compact silicon drift detectors allowed the integration of these detectors in the evacuable sample area, as the bulky heavy dewar with liquid nitrogen is no longer needed. So all features of analyzing samples in TXRF geometry with the well known advantages described in many papers are available and even improved by making experiments in vacuum without any problem.

2. Experimental

The TXRF module is attached mechanically by 4 screws to a tube housing from ITALSTRUCTURES [8]. All commercially available diffraction X-ray tubes can be inserted in the respective tube housing, and the module can be attached to all brands of tube housings on

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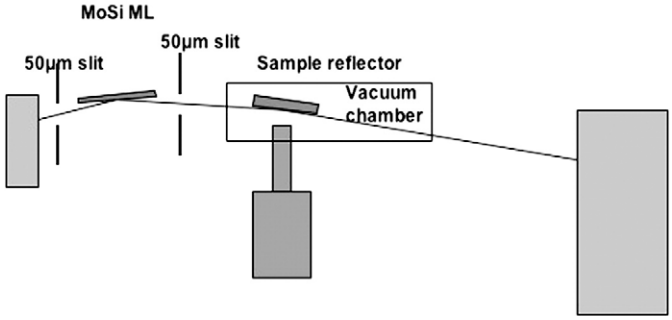

Fig. 1. Scheme of beam path.

the market by using simple adaptors. The X-ray tube is powered by an X-ray generator GNR C3K5, which allows remote control of voltage and current via RS 232 from PC. The Mo anode X-ray tube itself is a 3 kW model with an optical line focus 0.04×12 mm^2. The excitation spectrum from the X-ray tube is modi ed by a multilayer monochromator. The primary entrance slit of 50 m width is mounted close to the tube exit window. A multilayer made of 100 layer pairs of Mo/Si [9] with a spacing of 2d=4 nm monochromatizes the primary beam with high re ectivity around 80%. The monochromator holder unit allows the angle adjustment for Mo-K radiation according to Bragg's law. The 50 m exit slit is xed on the monochromator unit and acts both as beam stopper for the primary radiation passing over the surface of the multilayer and de nes the proper Bragg re ecting angle and thus the Mo-K energy. The air gap in the beam path after the monochromator unit to the entrance window is 5 mm. The beam channel in the sample holder unit is 10 mm wide and 8 mm high and is O-ring sealed on both ends by two Al-plates having a 20×5 mm opening in the centre. An 8 m thick Kapton® lm is glued on the openings for the beam on these Al plates representing entrance window on the upstream side and exit window downstream. Close to the entrance window there is a circular opening allowing to insert from top a round shaped 30 mm diameter re ector. After the loading a simple O-ring sealed cover plate is put on top. The re ector carrying the samples rests precisely on three steel balls de ning the re ecting plane inside the evacuable module which can be rotated and translated to align the system for the TXRF conditions. The detector itself is up looking towards the re ector carrying the sample. It is sealed on the bottom plate of the module by an O-ring so that the volume between top cover, sample and detector, and the complete beam channel can be evacuated.

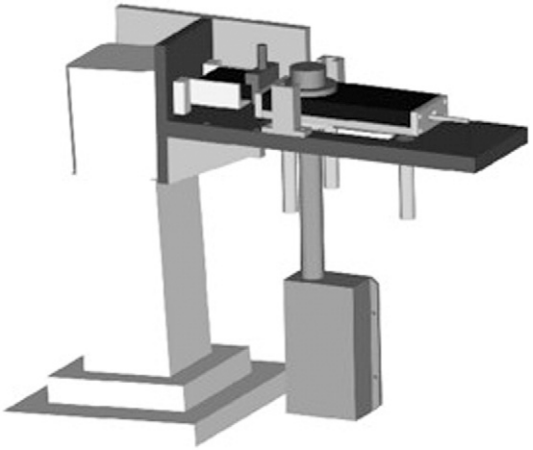

Fig. 2. Design sketch.

The detector in use is a 10 mm^2 Peltier cooled Si drift detector with 8 m Be window and a FWHM of 140 eV at 5.9 keV from KETEK [10]. The pulse shaper is an AXAS system integrated in the detector so that the output signal is directly fed into the ADC of the MCA. The data are stored and processed in the MCA of KETEK which is of same size as the detector. Finally the beam adjustment and control is done by a CCD camera looking on a ZnS screen as phosphor in the beam path to make the X-ray beam visible. The optical lens magni es the display and the video signal is transferred to the video board of the PC and can be observed on the screen. The proper adjustment is recognized by observing 2 separated beams — one is the direct and the second the re ected beam. At the down stream side of the Al casing of the CCD camera there is a Pb beam stopper to absorb the excitation radiation completely.

Fig. 1 shows the complete arrangement of setup. Fig. 2 presents the sketch of design details and Fig. 3 shows pictures of the new module.

The adjustment of the incidence beam on the re ector is done by 3 micrometer drives. The centre of rotation is set to the sample position so that angle dependent measurements of the uorescent radiation are possible in order to distinguish between lm and particulate type of samples deposited on the re ector. Also studies on implants

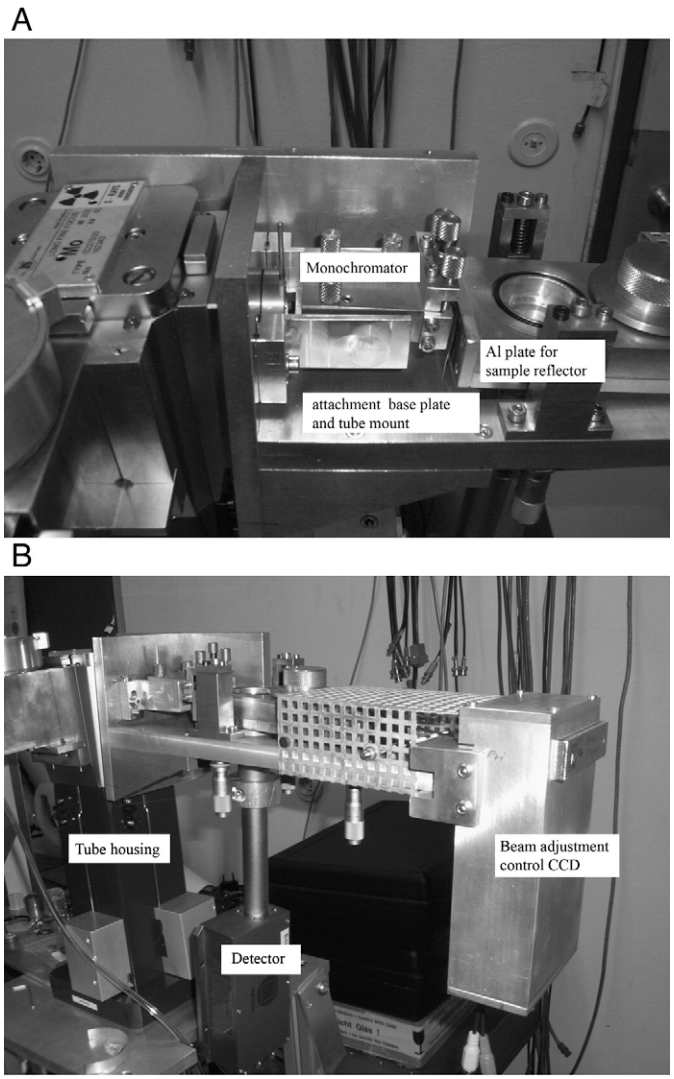

Fig. 3. A. Picture of the monochromator unit. B. Picture of the module with the camera attached.

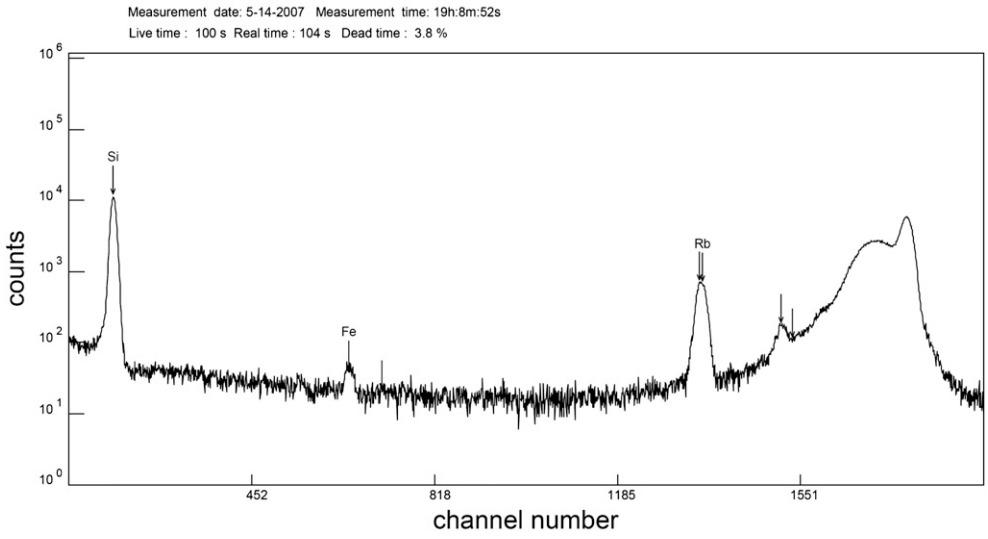

Fig. 4. Spectrum of a sample containing 2 ng of Rb, excitation conditions: 50 kV 40 mA 100 s.

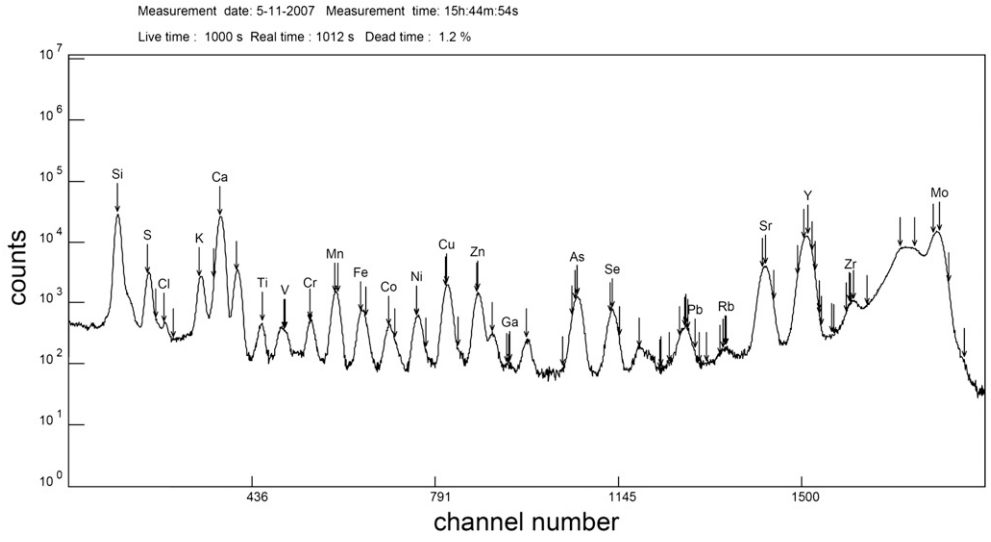

Fig. 5. Spectrum of SRM NIST 1640, trace elements in water, 10 l Containing trace element in the ng/g range.

could be performed using the angle dependence of the uorescence signal.

3. Results

The sensitivity for Rb–Ka was determined to be 75 cps/ng under operating conditions of 50 kV and 40 mA, the extrapolated detection limit for 1000 s counting time and vacuum conditions is 2 pg. Fig. 4 shows the respective spectrum. No Ar peak appears in the spectrum. Some Fe peak is also seen in the blank spectrum and might come from the detector. The spectra evaluation was done by the shareware WINQXAS [11].

Fig. 5 shows a spectrum of a Standard Reference Material NIST 1640 (trace elements in water) with element concentrations in the ng/g range; 10 l sample volume was deposited on the re ector and dried. The results of quanti cation of some elements shown in Table 1 are in good agreement with the certi ed values.

Fig. 6 shows the spectrum of an aerosol sample collected directly on a quartz re ector. These samples are collected with a Dekati-impactor© directly on the re ector for each stage corresponding to a certain particle size range. For the quanti cation procedure Y was added as internal standard to the sample. Due to vacuum conditions no Ar peak is found in the spectrum, the Al peak is clearly visible even with Mo-K excitation which con rms the very good performance for light element determination.

4. Conclusions

A simple low cost TXRF attachment module was designed and constructed. The system consists of a Mo 3 kW ne focus tube and a multilayer monochromator. The adjustment of the total re ection

Table 1
Results from the quanti cation of NIST SRM 1640-trace elements in water, selected element concentrations in μg/kg

	Certi ed	Measured
Cr	38.6±1.6	33.1
Mn	121.5±1.1	120.5
Ni	27.4±0.8	28.1
As	26.67±0.41	26.79
Sr	124.2±0.7	123.9
Pb	27.89±0.14	27.4

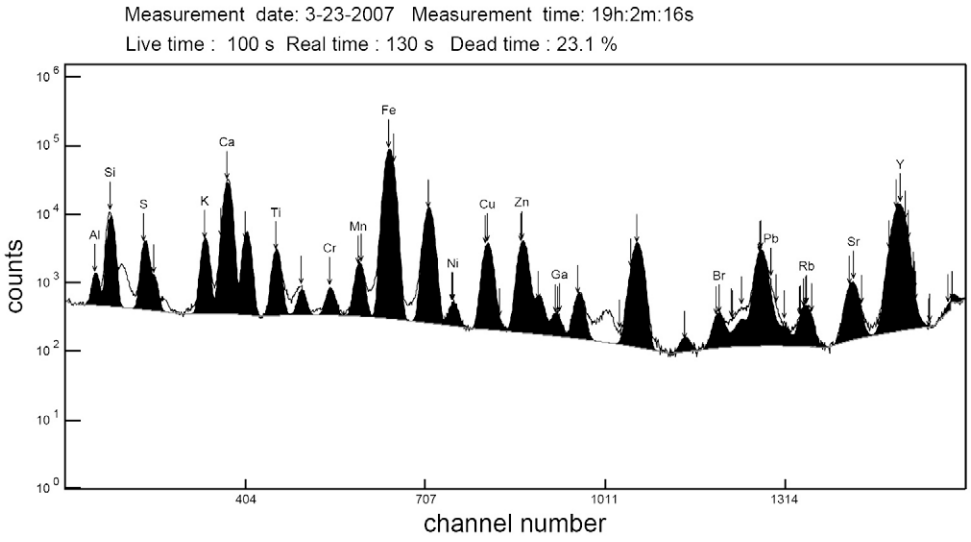

Fig. 6. Spectrum of an aerosol sample collected directly on a quartz re ector with a Dekati sampler. The peak on the right side of Si is the Ca escape peak, the peak below Pb-L is the sum peak of Fe and Ca–K line.

condition on 3 cm round re ectors is done with 3 micrometer drives with the pivot at the sample position allowing angle scans. The adjustment process for total re ection can be controlled by a CCD camera looking on a ZnS screen, the evacuable volume is small, and so a simple single stage rotation pump is suf cient. Due to vacuum conditions the background is considerably improved, thus low, and light elements can be determined by using a Silicon drift detector with 8 m Be window. The detection limits obtained are in the low pg range.

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