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The Microanalysis station at PWA

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1 INTRODUCTION

The use of storage rings as dedicated sources of synchrotron radiation together with the new developments of insertion devices have allowed, in recent years, the application of synchrotron radiation to the conventional methods of X–ray fluorescence (XRF). In addition, the so–called XRF induced by synchrotron radiation has given rise to the development of new spectrochemical techniques[1].

An experimental station for X-ray fluorescence studies has been installed at the PWA laboratory of the LNF. This station is mainly oriented to microanalysis, but it is possible to perform other techniques.

The apparatus existing at the beginning of 1991 consisted of an experimental chamber allowing conventional XRF (SRXRF) and total reflection X–ray fluorescence (TRXRF), but the latter was never implemented. The conventional system consists of a sample holder (3×6 cm) that can be positioned along the X,Y axis with a precision of 5 μm. The geometry of measurement is 90^{o} with 45^{o} of incident and take–off directions. At the entrance of the chamber two slits allow an orthogonal collimation.

The detecting system consists of a solid–state detector with a Si(Li) crystal (Silena), a high voltage source (ORTEC 478), an amplifier (ORTEC 572), and a multichannel analyzer (ORTEC 916).

2 WORK CARRIED OUT

2.1 First Stage Aims

Our first contact with the station was in March 1991. At the time the main problems were related to the poor detector resolution and to the positioning of the sample holder. There were other minor problems, such as poor and insufficient configuration of the electronic chain and of the data acquisition and processing.
Therefore, our first objective was to ensure that, after the second half of 1991, the station be capable of providing good and accurate results for both conventional XRF and total reflection XRF analyses, as well as be perfectly characterized regarding resolution, detection limits, measurement normalization, and data analysis.

2.2 Preliminary Improvements on the SRXRF Station

Special attention was paid to improving the detector resolution (in March 1991 it was 300 eV) so that it complied with the manufacturer's certificate of warranty (of the order of 189 eV). After work carried out on the signal, pulse shaping, collimation, and insulation, we improved the resolution to 185 eV. Later measurements showed that the resolution is strongly dependent on the power supply, which is three-phase and does not allow an autonomous supply. Figure 1 shows the behavior of the detector resolution as a function of the energy.
At this stage, the minimum detection levels were determined for different elements ($19<Z<33$), using thin sheets of pure elements of known thickness. Figure 2 shows the behavior of the minimum detection level with the atomic number.
As the average lifetime of an ADONE injection is about 3 hours, the photon flux is strongly dependent on time, as well as on some instabilities of the bunch orbit. It was then necessary to consider a normalization method for comparing different measurements. Using a V/F convertor and a pulse counter, the energy deposited in an ionization chamber on the line was taken as a normalization factor. Figure 3 shows the efficiency of the factor on a fluorescent Pb line.
Some difficulties regarding the sample–holder movements prevented irradiation in all points of the sample and prevented us from knowing the irradiation plane with precision. Thus, we performed repositioning and new alignments of the sample-holder system using a laser beam.

2.3 Preliminary Improvements on the TRXRF Station

The total reflection system is installed on the conventional system chamber. The detector is replaced by the goniometric system. The goniometer (which allows the critical angle to be determined) is driven by a stepper motor with a reductor system. Position reading is carried out by means of an encoder and a pulse counter with 4–min arc of precision. It was necessary to make improvements on the system because it was not working well.
This system was installed and aligned with a laser device, as for the conventional XRF setup.
The shutdown of the wiggler during the last week of July 1991 prevented us from checking the TRXRF setup and from making any future programmes.

2.4 Data Analysis

Good quantitative and qualitative analyses require a correct treatment of the measured spectra. The spectrum analysis package on the ORTEC 916 multichannel is specific for gamma spectroscopy. During the first stage of work, a programme for nonconventional spectrum analysis (smoothing, peak search and fitting) was developed[2]. The programme also allows conversion of ORTEC format spectra into other formats that include ASCII.
Later, one of the latest versions of the AXIL package[3] was implemented as an alternative system because it is highly optimized and allows fast analysis of complex spectra.
In relation to the quantitative analysis, a package allowing the chemical characterization, using simple conditions, of unknown samples was implemented. It has several correction models that carry out both fast quantitative estimation (without high precision requirements) and more accurate calculation using the fundamental parameter method[4, 5].

2.5 Difficulties Encountered

Most of the difficulties regarded the electronic chain, which was not quite appropriate for a synchrotron radiation source. There were also some problems connected with white noise on the detector signal, coming from the power supply.
At present, we are replacing some modules of the electronic chain in order to improve its performance.
The lack of time for performing optimization tests was a further difficulty.

3 EXPERIMENTAL

All the experiments so far carried out have been aimed at determining the characteristics of the system (sensitivity, stability, irradiation time, etc.). In addition, we have analyzed ways to prepare standards for quantitative analyses of our samples.

As regards basic investigation, some explorative measurements were performed to determine the sensitivity for detecting multiple interaction with an energy dispersive system like ours.

In the next sections we describe the measurements carried out.

3.1 Human Teeth

Measurements were made of teeth, in different positions. Each measurement took 600 sec of live time, which allowed good statistics for the major components, the minor components, and traces (see Fig. 4). The study of the internal structure and composition of a tooth by means of concentration mapping was a point of interest.

3.2 Environmental Dust

Measurements were carried out on environmental dust deposited on paper filters to detect the presence of some particular elements. Figure 5 shows a spectrum with the main elements detected.
These measurements together with minimum detection level determination allowed us to establish a strategy of standard preparations to perform quantitative analysis in the future.
Unfortunately, the experiments using the total reflection system were impossible to carry out (see Sec. 2.3).

3.3 Double Ionization

Explorative measurements were carried out on a pure sample of Ti, Cr, and Fe to determine the influence of the production of double K–shell vacancies on the fluorescent line intensities. Figure 6 shows an example of the results obtained. The double ionization edge energy as observed in the figure agrees very well with theoretical calculations.
The increase of the K–line intensity is due to the increase of the photoionization cross section, fluorescent yield coefficient, and the emission probability. It should be noted that this kind of interaction is currently ignored in the quantitative analysis of XRF spectra.

4 FUTURE WORK

4.1 Station

- The following modules will be incorporated in the electronic chain to optimize its performance: HV supply (ORTEC 659); amplifier (ORTEC 973); pulse generator (ORTEC 419); pulse counter (ORTEC 995); and PC/386SX with math coprocessor.

- The TRXRF techniques will be finally implemented. According to the results, the construction of a special chamber and the acquisition of a windowless detector (compatible with both chambers) will be studied.

- A more precise positioning system of the sample will be developed to study concentration mapping in thick and thin samples.

- Standards for quantitative analysis of thick and thin samples will be prepared using different techniques.

4.2 Research

4.2.1 Characterization of human teeth using SRXRF

- The presence of some elements in human teeth will be studied to establish a possible relation with their growth.
- Concentration mapping will be performed, and later a comparison will be made between the mapping and similar results from electron probe microanalysis.
- The same techniques as mentioned above will be used for bad teeth.

4.2.2 Characterization of environmental dust using SRXRF

- Quantitative analysis of environmental dust according to the available standards.
- Study of the oxidation state of light elements (Z<26) to determine the origin of the pollution.
- The above two points will be repeated using the total reflection technique.

4.2.3 Study of multiple interaction

- Extension of the double ionization measurements to more elements.
- Study of the influence of multiple transition (1 photon – 2 electrons ionizations and 2 electrons – 1 photon decay) on the XRF spectra.

5 CONCLUSIONS

In the microanalysis station it is possible to make qualitative and quantitative measurements on thick and thin samples using specific programmes. In order to perform quantitative analysis it is necessary to prepare appropriate standards.

We hope to install a new system that allows one to determine with precision the position of the beam on the sample. This will be important for all the analyses requiring spatial resolution.

The total reflection system has been aligned and all that remains to be done is to check the system and determine the detection limits.

Due to the actual configuration of the system, it is impossible to perform measurements on light elements in traces (Z<20). However, the sensitive system is quite good, as can be seen in Fig. 3.

Multiple interactions were detected successfully in an energy dispersive system, which means having the possibility of studying the influence of multiple interactions on the XRF spectra.

References

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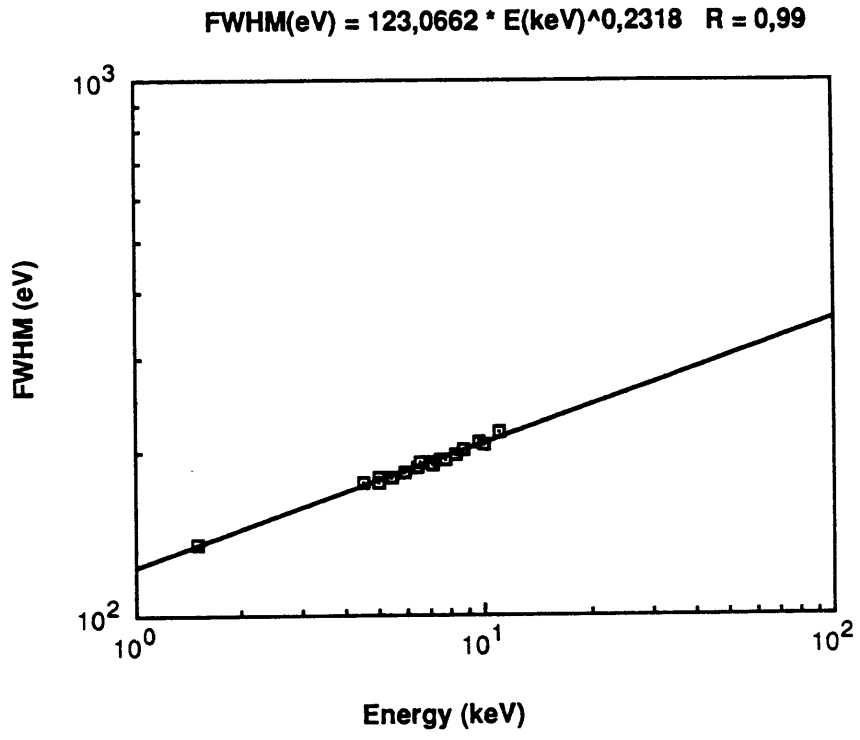

Figure 1: Detector resolution as a function of the energy

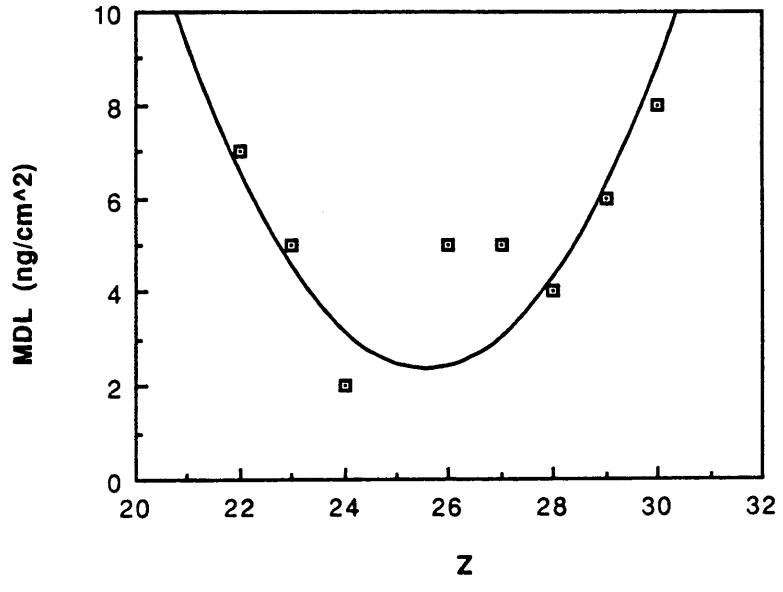

Figure 2: Minimum detection level with the atomic number

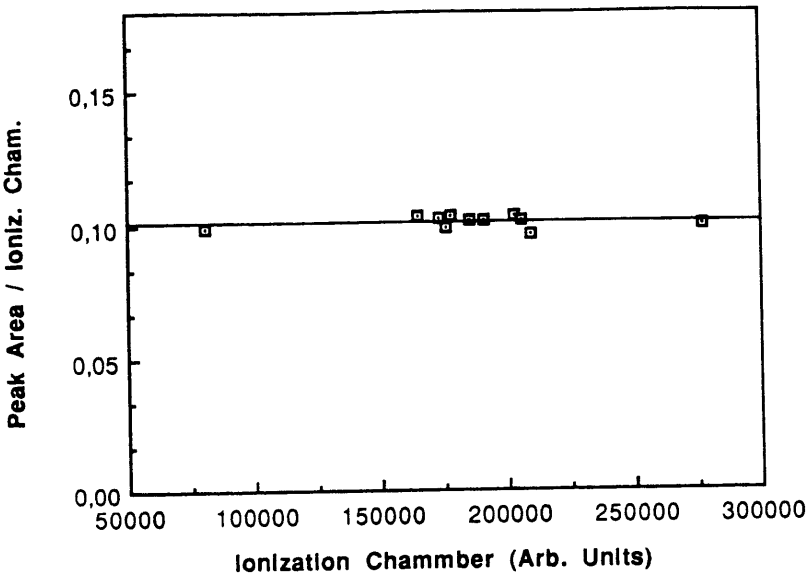

Figure 3: Normalization factor applied on a Pb L-line

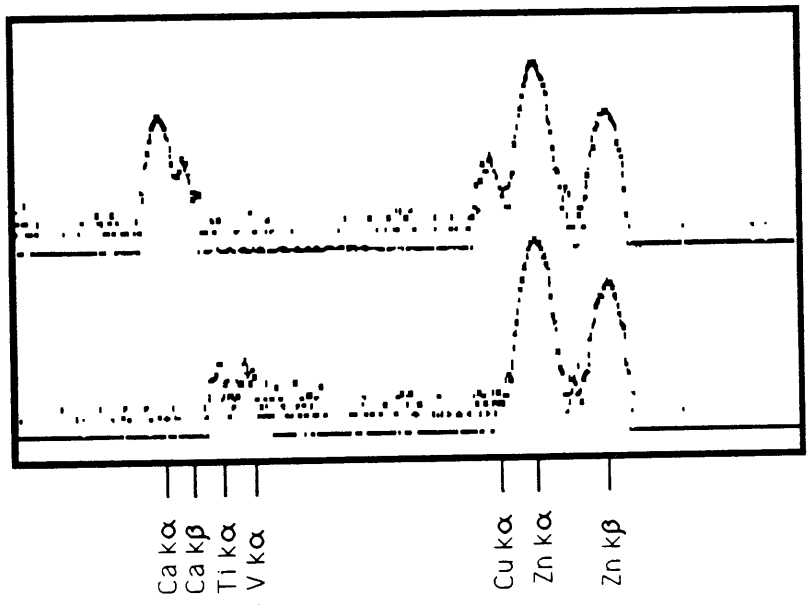

Figure 4: A comparison of the spectra obtained from the irradiation of a tooth in two different positions

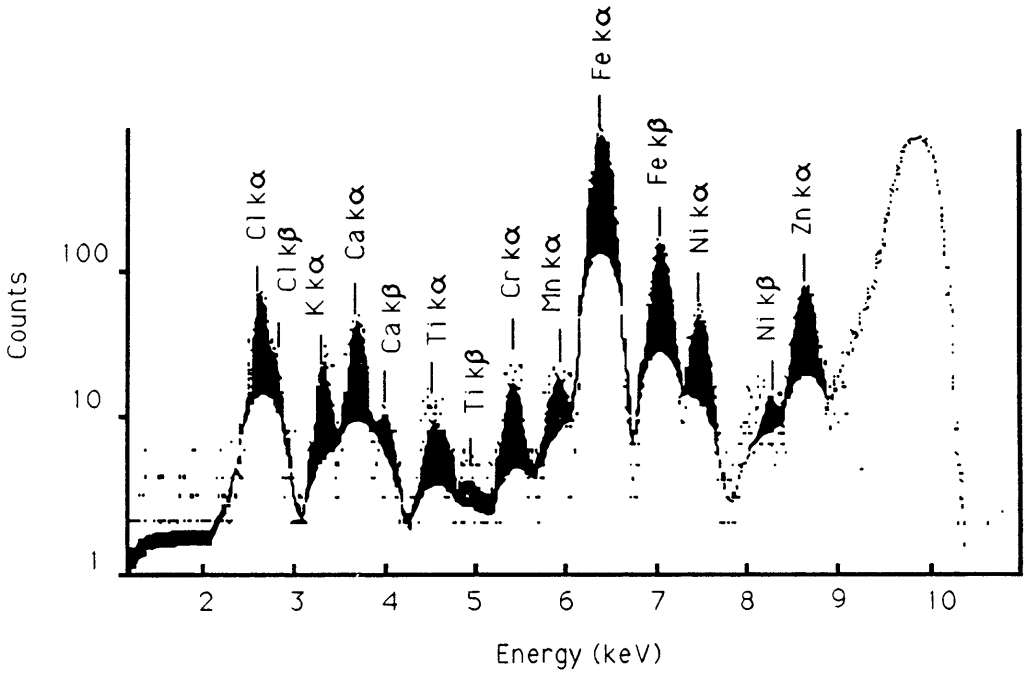

Figure 5: Spectrum obtained from an environmental dust sample

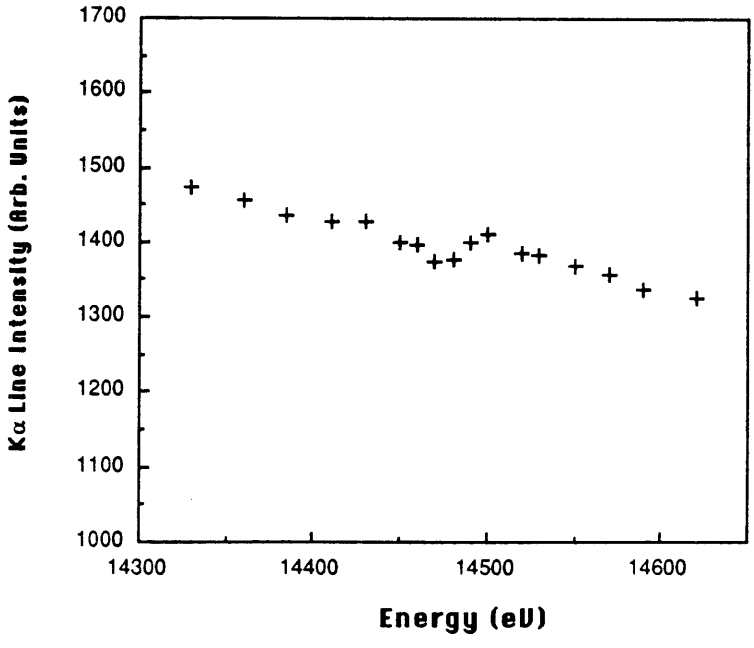

Figure 6: Evidence of double k-shell ionization in a Fe pure sample