

INTRODUCTION

X-ray fluorescence (XRF) analysis is a widely accepted analytical technique allowing fast, non-destructive determination of almost all elements in the whole concentration range. The XRF spectrometry has been developed along two paths: wavelength-dispersive spectrometry (WDS) and energy-dispersive spectrometry (EDS). Energy-dispersive systems provide an economical alternative to the multielement x-ray instrumentation with relatively simple installation and operating requirements, especially suitable for industrial and/or routine applications.

The commercial energy-dispersive systems are usually supplied with their proper hardware and software systems, supporting both, the data acquisition and data reduction procedures. Besides of this commercial equipment, there are lots of x-ray application laboratories equipped with a lower cost (about 10 times less) modular EDS, configured as a rule by an Si(Li)-detector, pulse processing electronics and a MCA interfaced to an PC/XT or PC/AT. However, their practical utilization has been limited by the traditional approach to the reduction and data evaluation. Unfortunately there is no commercial alternative to fulfill these needs.

To assist these laboratories IAEA has developed a general purpose QXAS (Quantitative X-ray Analysis System) [1] software extensively applied in different countries' x-ray laboratories. The QXAS package is run under a PC/AT or PC/XT (EGA monitor) and includes a sophisticated fitting of x-ray spectra as well as a choice of powerful quantitative analysis options.

The purpose of this work is to develop a PC based package for automatic industrial XRF analysis, compatible with the QXAS software system and designed to be used by an unexperienced operator for different analytical tasks - from the routine process control to the most demanding research applications.

The automatic x-ray fluorescence analysis package (ARFA) is carried out using proved techniques, developed and incorporated in multiple laboratory and industrial installations in metallurgy, ore processing, coal and nuclear power plants [2,3].

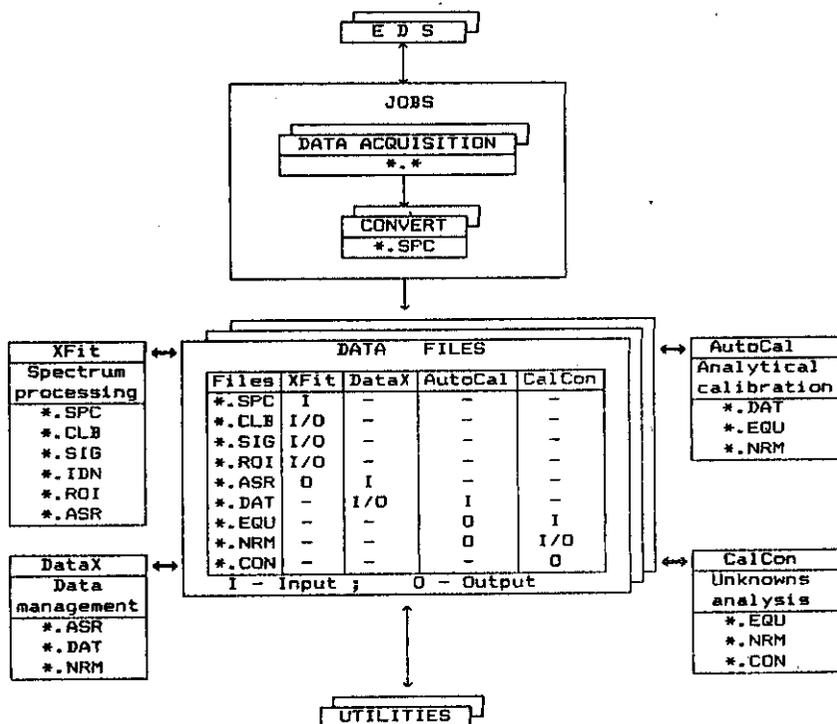


Figure 1.

GENERAL DESCRIPTION

The ARFA version EDS software system combines a modular EDS hardware with an automated data reduction software. Data can be accepted (off/on-line) from a wide variety of EDS systems via the appropriate data transferring and converting programs. Additional prior information is introduced through the keyboard.

The ARFA software architecture comprises five modules communicated via multiple data files (see Fig.1), i.e.

- XFit - x-ray spectrum processing program;
- DataX - calibration data management program;
- AutoCal - analytical auto-calibration program;
- CalCon - unknown analysis and accuracy check program;
- Jobs - includes data acquisition and converting programs.

The ARFA package can be run independently with its proper data acquisition and x-ray spectrum fitting programs, as shown in Fig.1, or as an industrial quantitative analysis version to the QXAS software system including DataX, AutoCal and CalCon.

The ARFA software is written in Turbo Basic, runs under DOS 3.1 or later, and uses a math co-processor for speed of execution.

EDS SYSTEM CONFIGURATION

The basic EDS system includes a Si(Li) detector with associated pulse-processing electronics, a XRF exciter, a multichannel analyzer (MCA) and a PC/XT or AT. There are two types of MCAs - a stand-alone MCA connected to the PC via standard interface and computer-based MCAs (NIM or CAMAC standard modules or direct Plug-In MCA cards) run under appropriate MCA Emulation software.

As an application example of this work the ARFA software system has been built around the buffer/stand alone MCA in CAMAC standard [4]. The package has been tested also with an EG&G ORTEC Multichannel Buffer (MCB), Canberra S100 MCA card and a stand alone MCA NOKIA.

The XRF exciter uses radioisotopes or low-power x-ray tubes to perform physical coding of 'hidden' chemical information in the sample being analyzed. Several geometry categories have been developed for multielement excitation (from Si to U) combining the direct and secondary excitation modes in an integral housing assembly [5,6]. The exciters use either point or annular radioisotopes or low-power x-ray tubes combining the regenerative monochromatic filters technique [7].

X-RAY SPECTRUM PROCESSING

Apart from the well documented advantages of EDS as the non-destructive and multielement character of analysis an important disadvantage is the theoretically limited resolution and respectively the high density of spectral components imposing a computer based analysis of spectra. Due to the complex nature of the spectra resulting from the spectral artifacts and the energy response of the electronics it is evident that the spectral data reduction is the most critical step in quantitative EDS analysis.

The qualitative and quantitative features of the peak unfolding programs suppose an automatic identification of elements present in the spectra, a removal of the escape peaks, a subtraction of the background and an extraction of the net peak intensities [8].

The XFit identify peaks by an automatic scan of the K and L lines of elements, a visual matching and identification. Line indicators may be called up by the element atomic number or its symbol. The selection of a particular peak energy gives a list of all possible elements closely matching that energy. A listing of the lines for each element can also be shown.

Once a satisfactory match is obtained it can be retained by pressing a [PrtSc] key which labels the major peak. All elements identified in a sample are stored on file (*.IDT) with the name of spectra for future qualitative analysis.

The next step in the information extraction flow is the background removal. The background can be modeled in several ways, manually by fitting a polynomial to the pre-selected points, automatically by digital filtering or calculated theoretically.

In any case the background interpolation techniques is quite arbitrary. According to the information theory, the well accepted assumption that the measurement contains the information to separate a peak structure from its underlying background continuum is not justified. Once the number of events accumulated in a channel of a peak region, it is impossible to identify the events belonging to a peak among the others. The approach generally accepted is to define spectrum region boundaries as close as possible by quite arbitrary statistical significance tests and then to assume a hypothetical simplified model's function.

The background removal in XFit is accomplished according to the explicit function proposed by Gunning [9], or by a polynomial fitting:

$$BC(x_l) = \begin{cases} b_n + (b_m - b_n) \cdot \frac{\sum_{j=n}^l Y(x_j)}{m} \\ \sum_{k=n}^l Y(x_k) \\ \sum_{n=0}^3 a_n \cdot x_l^n \end{cases} \quad (1)$$

Differently from other known spectrum analysis programs, proceeding only one spectral region or the whole spectra with a complicated background model's function or high degree of the polynomial, the XFit program for each output file (*.ASR) accepts up to 10 deconvolution windows processed by the background removal model (Eq.1). This reduces the information extraction uncertainty and improves considerably the numerical stability and accuracy of the background removal technique.

The peak-unfolding procedure is based on the description of each deconvolution window by a fitting function of the form:

$$Y(x_l) = \sum_{j=1}^{NP} A_j \cdot \exp\left[-(x_l - p_j)^2 / 2\sigma_j^2\right] + BC(x_l) \quad (2)$$

where $Y(x_l)$ is the spectrum data points at channel x_l ; A_j is the amplitude of the peak j , p_j is the centroid of the peak j , σ_j is the standard deviation or width of the peak j , NP is the number of peaks in the fitted region.

The background function $BC(x_l)$ is applied either before to the fitting procedure (Eq.1,a) or simultaneously during the fitting procedure (Eq.1,b). The least-square technique (linear or non-linear), applied to the function (Eq.2) find a set of parameters values which minimize the deviation (χ^2) between the mathematical function and the experimental spectra, i.e.

$$\chi^2 = \frac{1}{N - P} \cdot \sum_{i=1}^N \omega_i \cdot (y_i - Y(x_l))^2 \quad (3)$$

where y_i is the contents in channel x_l and ω_i is the weight function for channel i .

The peak's area are calculated as a integral of the normal (Gaussian) distribution, i.e.

$$AREA_j = \sqrt{2 \cdot \pi} \cdot A_j \cdot \sigma_j \quad (4)$$

The functional block-diagram of the XFit program is shown on

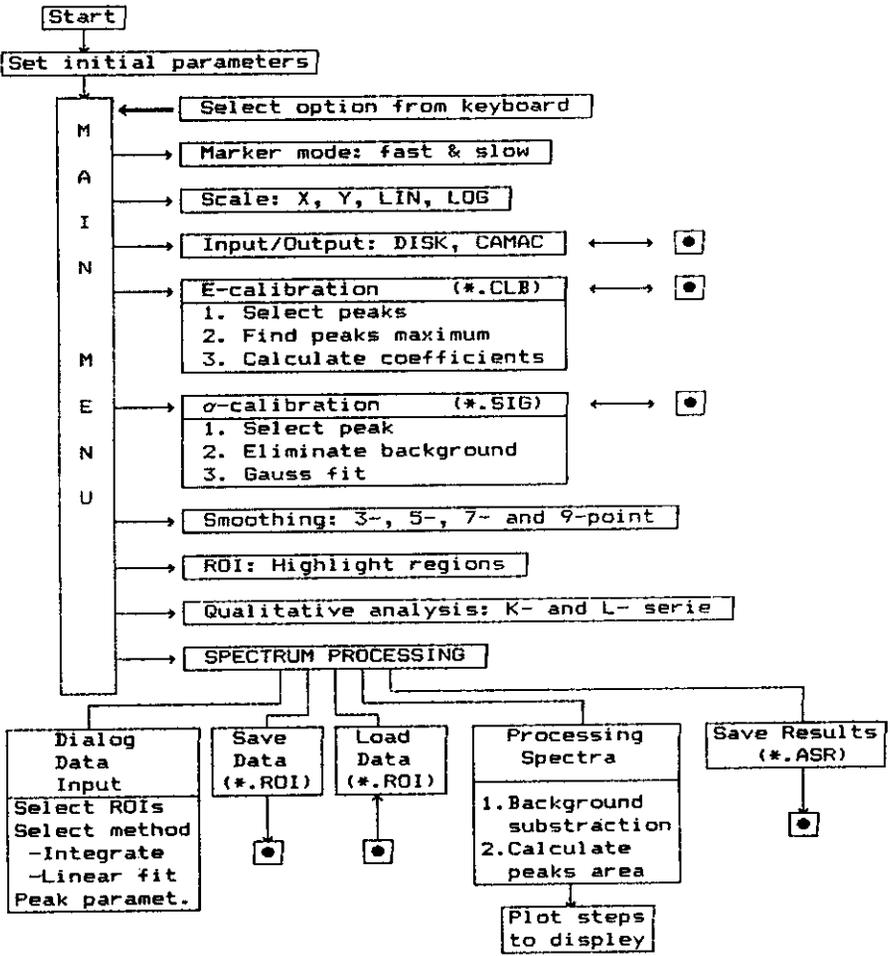


Figure 2.

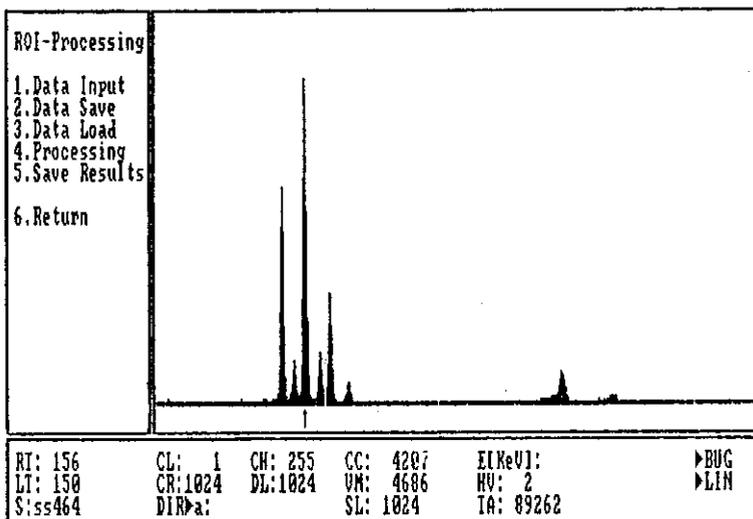


Figure 3.

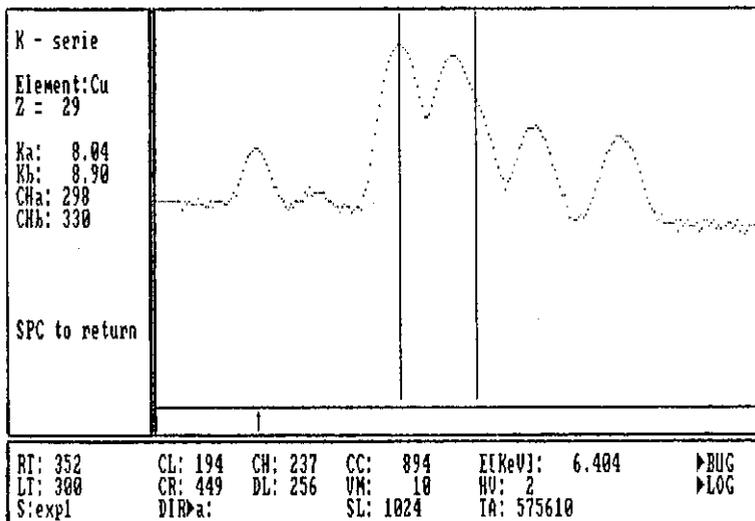


Figure 4.

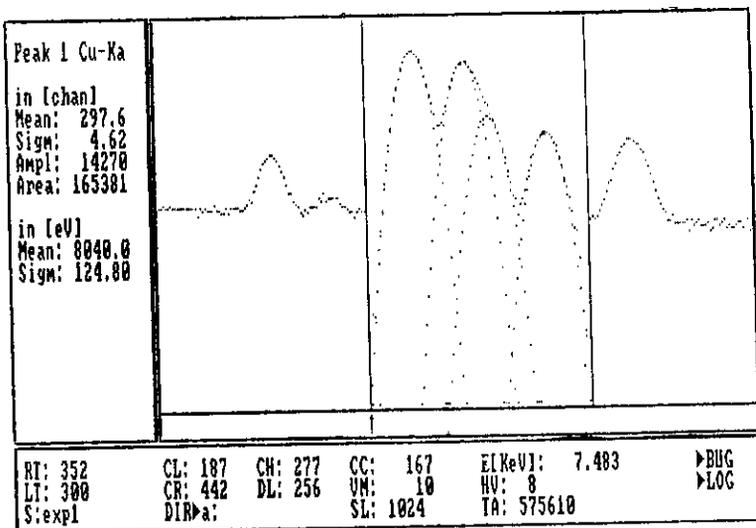
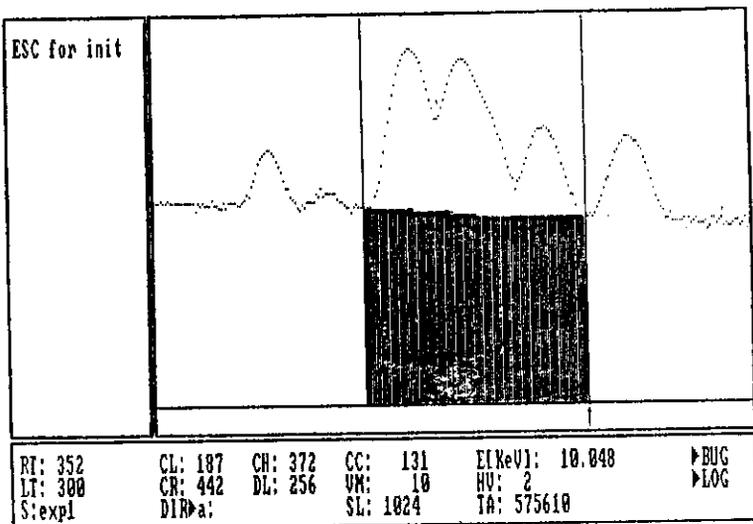


Figure 5.

Fig.2. The details of application of different deconvolution procedures are described in [9,10].

The general graphic design of the program includes three windows (spectrum, dialog and informatic) as shown in Fig.3. The next figures illustrate the main feature of the XFit program: Fig.4 shows an example of qualitative identification of Fe by the K-lines; Fig.5 illustrate a ROI processing algorithms - background subtraction and peak net area determination.

QUANTITATIVE ANALYSIS MODEL

The quantitative X-ray fluorescence analysis of unknown samples based on mathematical methods and models is the most commonly used technique in industrial and research XRF laboratories. This popularity is due to the simplicity of data processing algorithms and the possibility to realize them on the reasonably inexpensive computational facility. With minimal training, an unskilled operator could analyze quantitatively unknown samples if a prior reliable calibration with standards is made.

Empirical calibration models based on regression analysis generally calculate a set of empirical coefficients by a global compromise fit to all the available standards. Unfortunately, often the fitted parameters cannot possibly match all the standards exactly and miss some of the data points by more than the experimental error. That is way the planning of concentrations in the standards and the careful error analysis during the regression calculations is mandatory for achieving a reliable analysis via empirical correction models.

The most common approach to the multivariable regression methods uses a general fit of standard data to an equation in the form:

$$Y = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + \dots + a_n \cdot x_n \quad (5)$$

The values of calibration coefficients are calculated simultaneously and they are not independent. The least-square estimation of their values by multi-variable regression strongly depends on the initial distribution of the standard set. The well known empirical matrix correction models use basically the same mathematical procedure and differ by the weighting factors applied to the intensity/concentration data by means of appropriate transformations and substitutions.

The accuracy and reliability of analytical results depend on user's ability to select the appropriate set of standards and the most suitable analytical calibration model. The unknown concentrations may be calculated accurately only if the matrix composition of unknowns is close to that of the standards and to the assumptions of the selected calibration model. The commercial XRF suppliers point out that their responsibility is limited to the correct functioning of the mathematical algorithms and to the proper operation of the programs. The customer is responsible for the choice of standard samples, mathematical algorithms and calculation conditions. Therefore, in spite of the fact that the analysis and data processing of today's XRF systems are fully automated, the user assumes the responsibility for the accuracy and reliability of XRF results of unknowns. Those depend naturally on his theoretical knowledge and analytical experience.

The problems of incorrect approaches in the application of regression methods due to an unfortunate choice of interelement correction and to a poor range of calibration standards are discussed in [11]. It is shown how mathematically correct regression equations with acceptable goodness of fit can lead to totally wrong analytical results from unknowns. These facts are completely in accordance with the conceptions of the information theory mentioned above as the XRF empirical models generally have no physical meaning and the experimental information extracted from the standards is often insufficient to remove the uncertainty of the analytical model being built. The success depends on the complexity of the analytical problem as well as on the proper choice of standards and a mathematical model.

For this reason the analytical calibration model used in AutoCal has been based not only on the information from the raw intensity/concentration data of the standards, but also on a prior theoretical information about the shape of base-curves and on additional experimental information extracted from the scattered region of the spectrum, often denoted as a "matrix dependent" [12]. The program AutoCal includes a fixed or optimizing mode of generation of analytical curves especially suitable for non-experienced operators.

Taking into account the theoretical considerations of our quantitative analysis model, the basic shape of intensity/concentration curves for a pseudo-binary mixture can be presented as a hyperbolic curve with positive or negative

deviations from the linearity depending upon the relative absorption coefficients of both constituents [11]. Rasberry and Heinrich [13] pointed out, however, that the curves for enhancement cannot be adequately described by a hyperbolic function, and they proposed a new model in which predominant absorption, or predominant secondary fluorescence, was treated separately. The base-curve fitting procedures generally apply a polynomial approximation (up-to second degree) of the raw intensity/concentration data [14], i.e.

$$C_{\alpha}^{\circ} = A_{\alpha} + A_1 \cdot I_{\alpha} + A_2 \cdot I_{\alpha}^2 \quad (6)$$

The interelement effects in a typical multicomponent matrix spread out the shape of basic calibration curves in a multidimensional space of intensity/concentration relationship. If more than three matrix dimensions (elements) are used, the geometric intuition of the model is lost. That is why, instead of preceding to a simultaneous calculation of all calibration coefficients, the AutoCal applies absorption/enhancement matrix corrections to the theoretically predicted by the base-curves concentrations using either linear or non-linear least-square stepwise procedures [15].

Combining the intensity matrix correction models with the theoretical base-curve relation (Eq.6) the following quantitative analysis models have been obtained and incorporated in AutoCal:

1. Linear or additive intensity correction model:

$$C_{\alpha} = C_{\alpha}^{\circ} + \sum_i^N K_{1i} \cdot I_i \quad (7)$$

2. Full linear/quadratic/multiplicative intensity correction model:

$$C_{\alpha} = C_{\alpha}^{\circ} + \sum_i^N K_{1i} \cdot I_i + \sum_j^M K_{2j} \cdot I_j \cdot I_i \quad (8)$$

3. Linear and multiplicative intensity correction model:

$$C_{\alpha} = C_{\alpha}^{\circ} \cdot \left(1 + \sum_i^N K_{1i} \cdot I_i \right) \quad (9)$$

4. Lucas-Tooth and Pyne intensity correction model:

$$C_{\alpha} = A_{\alpha} + A_1 \cdot I_{\alpha} \cdot \left(1 + \sum_i^N K_{1i} \cdot I_i \right) \quad (10)$$

5. Exponential (ORTEC) intensity correction model:

$$C_{\alpha} = C_{\alpha}^{\circ} \cdot \exp \left(K_{\alpha} + \sum_i^N K_{1i} \cdot I_i \right) \quad (11)$$

where $i \neq \alpha$.

The choice of calibration model depends on the accuracy

desired by the operator, the type of material being analyzed and the availability of standards.

The second basic assumption of the AutoCal analytical calibration procedure is the use of information from incoherent and coherent scattered radiations or the so-called method of standardization with scattered X-rays [16]. As pointed out by many authors, up to 50% of the total counting rate is due to the backscattered radiation which is a matrix dependent. That is why including scattered peaks in the matrix correction model can successfully simplify the calibration equations and reduce the number of required standards. The simpler the calibration equation, the better is the reliability of analytical results on unknowns.

Different versions of standardization with scattered X-rays are in common use: the analyte-line vs. scattered target-line (I_a/I_{scat}), the analyte-line vs. coherent/incoherent scattered ratio $I_a / (I_{coh.} / I_{inc.})$, the analyte-line vs. coherent and incoherent target-lines $I_a / (I_{coh.} + I_{inc.})$, etc.

The theoretical study of I_a / I_{scat} ratio [17] shows that both intensities depend identically on the matrix composition of the sample only for a narrow concentration range limited at low and high levels. Generally, it was shown that the dependence of I_{scat} on the mass absorption coefficient of the matrix (μ_m) is more significant than that of I_a on μ_m . Therefore if one chooses for calibration purposes analytical parameters as

$$I_a / (I_{scat})^n \quad (12)$$

or

$$I_a / (I_{coh.} / I_{inc.})^n \quad (13)$$

with $n \neq 1$, then for $n \approx n_{opt}$ the intensity ratios would be constant with the change of matrix element concentrations.

Analogically the applicability of the third relation has been extended by introducing weight coefficients k_1 and k_2 , i.e.

$$I_a / (k_1 \cdot I_{coh.} + k_2 \cdot I_{inc.}) \quad (14)$$

The default values of the optimization parameters used in AutoCal are: $n = 1$, $k_1 = 0.1$ and $k_2 = 0.9$. The theoretical limit for n is less than r_a ($r_a =$ absorption-edge jump ratio); the coefficient values k_1 and k_2 are optimized experimentally according to the excitation parameters and the matrix composition.

As already shown in Fig.1 the quantitative analysis features

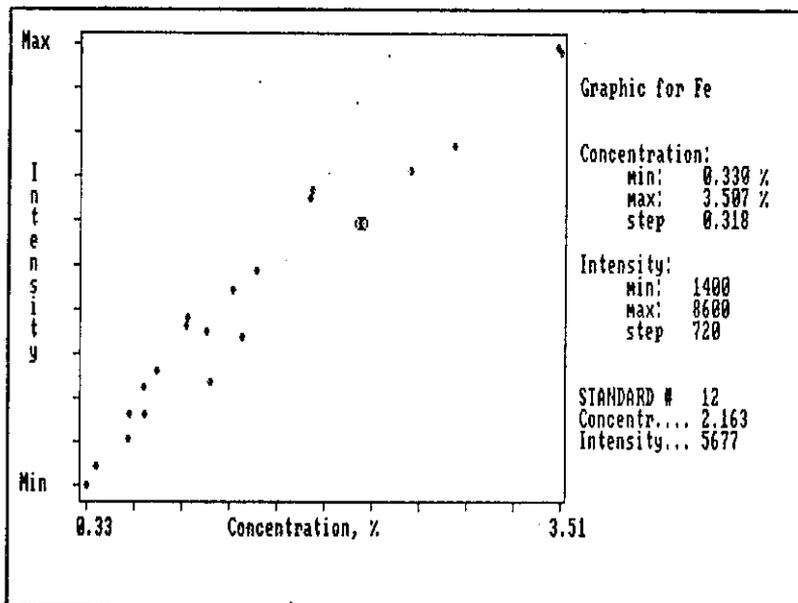


Figure 6.

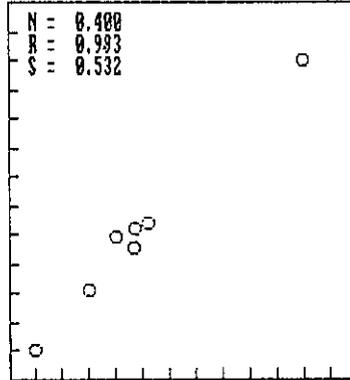
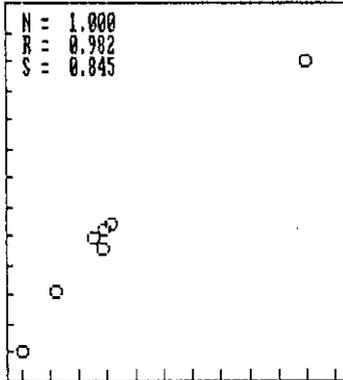
of the ARFA package are supported by DataX, AutoCal and CalCon as menu selected programs.

The data management program DataX creates a calibration data base using intensity files *.ASR and concentration data. Different plot and data management options are provided to control the quality of calibration standard data. Fig.6 shows an example of a VDU plot of intensity/concentration data file.

The analytical calibration program AutoCal optimizes and generates working curves for each analyzed element. The printout in Fig.7a,b illustrates the optimization procedures of the analytical parameter and the working curves. The calibration protocol obtained is stored on disk for further use by the unknown analysis program CalCon. Before calculating the concentration values CalCon tests the compatibility of the unknown sample to the matrix composition of the standard set and the assumptions of the analytical model have been chosen.

ANALYTE : Cr RATIO TO : Fe

ANALYTICAL PARAMETER : Cr/Fe^M



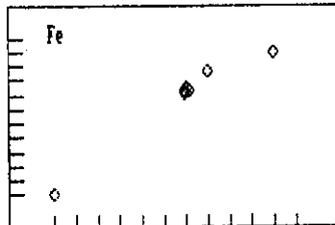
PRESS <ESC> TO QUIT! / <ENTER> FOR A NEW POWER!

OPTIMIZATION

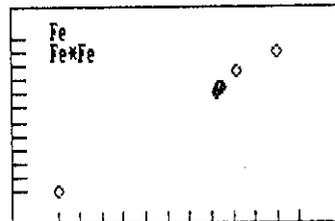
STEP # 2 !Fe -> Fe/Ni^ .3

Start MODEL	Correl COEFF.	Test MODEL	F-coeff. < 10 >
Fe		Fe	
Fe*Fe		Fe*Fe	
Mn	.53	Mn	.75
Fe*Mn	.207		

Base Curve



Matrix Correction



HIT ANY KEY

Figure 7.

CONCLUSION

The developed automated x-ray fluorescence software system ARFA, designed for both research and industrial needs, requires a minimum user's training in order to be operated and to perform an accurate quantitative analyses. The modular design of the software package allows easily to extend its performance and to incorporate it in almost all personal computer-based EDS systems.

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