USE OF X-RAY FLUORESCENCE FOR THE ANALYSIS OF SOME LOCAL CRES

A Thesis Submitted in Partial Fulfillment of the requirement for the Degree of Master of Science in Physics

By

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الخلايا النباتية

ناناً، كان نحل الخلايا الجزيئية، فرع إثر بيئة خارجية فضفاضة أو ترس الخلايا، 
الأوردة، وتم تشفير إدخال بعض الألياف الخلايا مذ الانتشار في الواد، 
ب дорог، والعمل النموذجي، مثبط الفيتو، عالم الحروفي المتحف، يعتمد على اختراق الميلاء 
السنية، والتحلل بالمحيط النوى بواسطة الخوليد الخضري، وينتشر بالمادة جوانب التحليل 
النفسي، إحداهما تمثل عن الأثرية، ويصري عناقيد وأطرواف على استخدام مولدات الأشعة 
السنية المغلقة.

في هذا البحث حصلت محاولة للتحليل مصمم الخلايا الجزيئية النباتية ذات الخلايا السنية، أما بإنتاجات 
القبضة، في الحزام، السيليكون والمطهر، ودردشة الكروم والدهب، بتداخلها 
الصفقات، إحدى الخلايا السنية، وتلميع الكروم، وتلميع الكروم والدهب في الميال، 
في جهد من محاولة الشبيه، وتلميع طريقوتها من هذا النوع، للتحليل سريعة، ويوفره على 
لديلاء، العصبيين حيث آخذوها كهير على التحليل النكش بواسطة الحواسيب، وأخرى باستخدام السينار، 
الشبيه بالعنبة السنية المغلقة، وطورهما يمكن تحقيقهما، في الإنشاء، أو باستخدام أطرحة أخرى.

ولد كرفس كذلك للتحليل الم הקר، من حيث أنه عمر كارد وذات قضاء اقتصادية عالية.

وقد أظهرت طريقة فعالة للتحليل سريعة ل vessى الذهب، 
وأثبتت ذات الخلايا في تحليل الشعر الكروم بالميال، ودلي stati- 
التحليل، يحضر الكروم السيليكون، إلا أنه لم يكن ناجحاً كبيراً وقد أظهر التحليل بواسطة 
الإجابة، لإجماليات، إحدى الشبيهة، وذات خلايا، ونتيجة لاستخدام طاقة وآليات، 
أيمانية في الحزام.

وأوصي باستخدام أتوت معن، في البدء بالتحليل النهاي ذات الخلايا المنخفضة عن طريق 
الانهيار السني المغلق أو بدلاً، كذلك يتم التحليل بواسطة التحليل، مع، في البدء على طرق، 
السيروتونين،
ABSTRACT

Earlier the analysis of geological samples was either carried out through tedious chemical methods or done abroad, with high costs in hard currency. Recently some modern nuclear-based analytical techniques have been introduced into the country, at the Nuclear Science Laboratory, Department of Physics, University of Khartoum, including X-ray Fluorescence (XRF), Neutron Activation Analysis (NAA) using the Neutron generator. Two XRF systems are presently available: one based on isotopic source excitation and the other on tube excitation.

In the present work an attempt has been made for the analysis of some local geological samples of relevance to the national needs, namely Cr, Fe, Mn, Al, and Au using the XRF technique. Special attention was dedicated to the analysis of Cr and Fe in chromite samples from Ingasmara region. The XRF methods were developed from the fast and reliable analysis of these two elements: one based on NBS (USA) software and the other using mathematical methods to account for matrix absorption effects in the samples. The two methods were comparable, with the latter slightly faster.

A lot of attention was also dedicated to the analysis of Au, this being an important element, with high economic value. A reliable method has also been developed for the reliable and relatively fast analysis of Au.
The analysis of Na was similar in procedure to Cr. Some effort was also made for the analysis of Al and Si, though without much success. Problems were encountered in the analysis of these two elements because of their low energies (1.5 and 1.7 keV, respectively) and their possible absorption in the sample itself, in air and the Be window. It is recommended to work in vacuum chamber for XRF analysis of these two elements. Alternatively, (NAA) should be considered using the Neutron generator.
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لقد كُرس كذلك لتحليل عصير الدم، فضلاً عن فحص الدم، والذي كان يشمل اختبار الكريات البيضاء والمزاج. راى واسعًا نطاقًا بموجب قانون لمدة التحليل، إذ يتضمن الاختبارات المخبرية دائمة للتواصل مع المشاكل المحتملة من طريقة.

لا يوجد توضيح محدد أو مسبوق فيما يتعلق بالتحليل بواسطة الفلترة الخلوية من طريقة الميكوف.
ABSTRACT

Earlier the analysis of geological samples was either carried out through tedious chemical methods or done abroad, with high costs in hard currency. Recently some modern nuclear-based analytical techniques have been introduced into the country, at the Nuclear Science Laboratory, Department of Physics, University of Khartoum, including X-ray Fluorescence (XRF), Neutron Activation Analysis (NAA) using the Neutron generator. Two XRF systems are presently available: one based on isotopic source excitation and the other on tube excitation.

In the present work an attempt has been made for the analysis of some local geological samples of relevance to the national needs, namely Cr, Fe, Mn, S, and Au using the XRF technique. Special attention was devoted to the analysis of Cr and Fe in chromite samples from Ingassana region. Two XRF methods were developed from the fast and reliable analysis of these two elements: one based on NBS (USA) software and the other using mathematical methods to account for matrix absorption effects in the samples. The two methods were comparable, with the latter slightly faster.

A lot of attention was also dedicated to the analysis of Au, this being an important element, with high economic value. A reliable method has also been developed for the reliable and relatively fast analysis of Au.
The analysis of Mn was similar in procedure to Cr. Some effort was also made for the analysis of Al and Si, though without much success. Problems were encountered in the analysis of these two elements because of their low energies (1.5 and 1.7 kev, respectively) and their possible absorption in the sample itself, in air and the Be window. It is recommended to work in a vacuum chamber for XRF analysis of these two elements. Alternatively, (NRA) should be considered using the Neutron generator.
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The continuing interest in trace elements has stimulated the development of several powerful analytical techniques for their detection and quantitative determination. One of these is x-ray fluorescence (XRF), where a source of x-ray photons is used to study the elemental composition of materials. Absorption of these photons by the photoelectric effect produces vacancies in the inner electron shells of the atoms of material, followed by the emission of characteristic x-ray of the elements present. The peaks in x-ray spectrum indicate what kind of atoms are present, while the number of counts (the area under the peak) is related to the number of the atoms in the sample, allowing the quantitative measurements to be made. Moreover, the method gives information about the elements present in the sample irrespective of their state of chemical combination or the phases in which they exit [1]. The wide application of the XRF analytical method may be attributed to the following:

1. Availability of strong exciting radioactive sources which can produce monochromatic x-rays.
2. Development of reliable Li-drifted silicon detectors.
3. Relatively low prices of the complete system used in XRF analysis. The sensitivity of the method depends on the energy of
characteristic X-ray of the elements analyzed and it increases as the ratio of the absorption edge energy of the element analyzed to the excitation energy from the source increases.

Energy - Dispersive X-ray Fluorescence (EDXRF) spectrometry is an established technique for qualitative and quantitative elemental analysis. It is presently routinely used in the analysis of various samples, including environmental samples, biological samples such as plants, human and animal tissues, geological samples, etc.

In this study, the XRF technique is applied for the analysis of some geological samples. The geological samples, which had been obtained from south eastern regions of the Sudan, have been analyzed for Al, Si, Cr, Mn, Fe and Au contents. The samples, usually in rock and soil form, were first crushed, then ground into fine powder, and finally pressed into pellets.

Measurements were made for a large number of samples. For Al and Si, which are light elements, a secondary target of Fe was used. For Cr, Mn and Fe, which are medium elements, a Zr as well as Mo secondary target was used. For the heavy element Au, the L lines were excited using Mo secondary target. The analysis of Cr and Fe was also attempted using an alternative method of analysis using mathematical regression coefficients, for comparison.
[1] Photo-electric effect.
[2] Incoherent (Compton) Scattering,
[3] Coherent (Rayleigh) Scattering
[4] Pair Production

The interaction of importance in the energy range of interest for XRF are the first three ones. Pair production is ignored since it is only important at energies above 1.02 MeV.

The photo-electric effect is the absorption of a photon by an atomic electron and consequent ejection of the electron, leaving the atom in an excited state. De-excitation of the atom is accompanied by electron transitions and emission of characteristic x-rays.

The photo-electric effect is more dominant at low energies. In this inelastic process the electron is ejected with a kinetic energy given by:

\[ \text{k.E} = h\nu - \text{B.E.} \]

where \( h\nu \) is the incident photon energy and \( \text{B.E.} \) is binding energy of the orbital electron.

The photo-electric effect is a typical resonance effect, with the greatest probability occurring when the photon energy is equal to the binding energy of the electron in a corresponding shell. The photo-electric absorption is then maximum. [3]

The Compton effect (or incoherent scattering) is the result of the impact of an incident photon (\( E = h\nu \)) on an electron loosely bound to the atom. The
function of the size of the pulse from the detector. The highest energy peak in the spectrum occurs at the energy of the incident excitation and is due to X-rays that Rayleigh Scatter from the sample into the detector. The broad peak at a slightly lower energy is due to the inelastic Compton Scattering in the sample. The low energy continuous distribution is due to Compton Scattering in the detector. X-ray fluorescence signals are represented by the various peaks occurring at energies well below the high energy Compton and Raleigh Scatter peaks [2].

2.3 \textbf{Characteristic X-ray Production:}

The production of the characteristic x-ray lines follows the excitation of the target atom by an incident photon as shown in fig (2.2a). As a result of absorption of the photon energy, one or more electrons from the inner atomic shells is removed. This is shown in fig (2.2b) [3].

In the process of de-excitation, that is when the resulting vacancy is filled by an outer shell electron, X-rays whose energy is characteristic of the particular atom, are emitted. This is shown in fig. (2.2c). Detection of such x-rays is the basis of x-ray fluorescence technique. The energy of the photon is given by [3]:

\[ E = h\nu \]

and is equal to the energy difference between the level of the vacancy and that of the electron.
Fig. 2.2.a The photon is absorbed by a K-shell electron.

\[ E_e = E_k - E_b \]

Fig. 2.2.b The electron is ejected with an energy \( h\nu - E_b \) where \( E_b \) is the K-shell binding energy.

Fig. 2.2.c An L-shell electron fills the vacancy. \( E_k \) is K-Xray energy.

Fig. 2.2.d Emission of Auger electron from the L-shell.
filling that vacancy. This is expressed as (3):

\[ E_X = E_o - E_i \]  \hspace{1cm} 2.3.2

Where \( E_o \) is the energy of the outer-shell and \( E_i \) is the energy of the inner-shell. Fig (2.2d) represents Auger electron emission, whereby the emitted x-rays given by eqn. (2.3.2) can further excite the atom leading to emission of Auger electron.

2.4. Selection Rules and Characteristic Lines:

In classical mechanics, all higher level electrons can potentially transfer to lower levels to fill vacancies. In quantum mechanics the initial and final energy levels in any radiative transition must obey the following selection rules:

\[ \Delta n = 1, \Delta l = \pm 1, \Delta j = 0 \text{ or } \pm 1 \]  \hspace{1cm} 2.4.1

Where \( n, l \) and \( j \) correspond to the principal, orbital and total angular momentum quantum numbers, respectively.

The transition predicted by the selection rules are shown in fig. (2.3), (3).

If the vacancy is created in the k-shell of an atom, the characteristic k-x-rays are liberated when that vacancy is subsequently filled by the upper level (L or M) electrons. If the electron comes from the L-shell, then a \( K \) - photon is produced whose energy is equal to the difference in binding energies of K & L shells. If the filling electron
Fig (2.3) Partial energy level diagram showing the origin of the main lines in the K and L spectra.
originated in the 4-shell instead, then a $\gamma$-photon is produced by transition from the M-shell to the k-vacancy and so on. [4]

Because their energy is greatest, k-line x-rays are generally of most significance. Their energies increase regularly with atomic number of the element. This relation is found by Noddle (1913), in which the wave number for any particular line is expressed as:

$$\nu = R(z - \alpha) \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Where $R$ is a probability constant, $z$ is the atomic number of the element, $n_1$ & $n_2$ are integers characteristic of the particular line, $\alpha$ is a screening factor which is needed because orbital electrons in outer shells will be partially shielded from the nuclear charge.

2.5. Auger Electron:

In spite of the high probability for K-shell vacancy production, not every transition of an outer electron from the atom to the inner vacancy results in x-ray emission. There is a probability for a certain non-radiative transition known as Auger transition. [5]

In an Auger transition, the deexcitation energy is transferred to one of the atomic electrons, which is then emitted instead of a photon [Fig 2.26]. Actually, it is a direct energy transfer process, but it can be imagined that a photon is produced in
the first instant, which collides with the electron in its way out of the atom. These electrons have a line energy spectrum characteristic of the element concerned, but their energies are very small and may be expressed as [3].

$$E_R = (E_i - E_k) - E_k \quad \quad \quad \quad \quad \quad \quad 2.5.1$$

Where $E_k$ is the binding energy of the electron, and $E_i$ and $E_k$ are the involved energy levels.

The most important effect of the Auger electrons on the XRF analysis is the fact that they reduce the number of x-ray photons to be expected of the particular source.

2.6. Fluorescent Yield:

One consequence of the Auger effect is that the lines in a given series are not as intense as would be predicted from the number of vacancies created in the associated shell. Thus we can define the K fluorescent yield, $W_k$, as the number of photons of all lines in the k-series emitted per unit time divided by the number of k-shell vacancies created during the same time. [6] i.e

$$W_k = \frac{\sum (n_{k})}{n_k} = \frac{n_k + n_k + n_k + n_k + \cdots}{n_k} \quad \quad \quad \quad 2.6$$

Where:

$W_k$ is k fluorescent yield,

$n_k$ is rate at which k-shell vacancies are created, and

$n_{k1}$ is rate at which photons of spectral line
are emitted. The L and M fluorescent yields, \( W_L \) and \( W_M \), are defined similar to \( W_K \). Auger electron yield may therefore be defined as the ratio of the number of Auger electrons produced to the orbital vacancies created in the same time i.e., Auger electron yield = \( I - W \).

Where \( W \), the fluorescent yield, is approximated by relation:

\[
W = \frac{Z^4}{(A + Z^2)} \quad \text{................. (2.7)}
\]

Where \( Z \) is atomic number, and \( A \) is constant with \( A = 10^6 \) for K x-rays and \( A = 10^7 \) for L x-rays. The K and L fluorescent yields are shown as a function of \( Z \) in Fig. (2.4).
Fig. 2.4 Fluorescent yield as a function of atomic number [Ref. 3]
3.1. Introduction:

In the XRF analysis technique, the sample to be analyzed for elemental composition is irradiated using x-ray tube. The characteristic x-rays of the elements present in the sample are produced during the irradiation and detected by a Si - (Li) detector. The charge collected by the detector provides an electrical signal proportional to the x-ray energy emitted. This signal passes to a pre-amplifier mounted with the detector, which integrates each detector signal to produce a voltage pulse proportional to the charge. This pulse is then amplified and shaped by a linear amplifier. The amplified signal is processed and displayed on a Multi-Channel Analyzer (MCA) which is connected directly to a computer where the x-ray spectrum is analyzed. A block diagram of the experimental set-up is shown in Fig. (3.1). An enlarged view of the XRF spectrometer system for tube excitation is shown in Fig. (3.2).

3.2. Si(Li) detector:

It is a type of semiconductor detector, with energy gap less than 3 eV between conduction band and valence band, and containing impurities with energy levels close to conduction band. Thus, it is easier to remove electrons to the conduction band.
Fig. (3-1) Experimental set-up of the XRF system
In Si(Li) detector lithium ions are diffused into surfaces of p-type silicon with acceptor type impurities, which produce positive carriers, forming and n-type region, as shown in Fig. (3.3). When a high voltage is applied lithium ions drift through p-type material, then equilibrium condition is established, where lithium ions pair with atoms of dopant material creating a region of intrinsic properties. The detection window is usually made of thin Be which allows most of x-rays of energy 0.6-60 keV to pass through. Each x-ray entering the detector gives rise to a number of ion pairs producing a charge pulse whose amplitude is proportional to energy deposited in the detector. This charge is swept from the detector by the high voltage applied across it. The Si(Li) detector used in this work is PET type.

3.3. Energy Resolution:

Energy resolution is an important performance index for an XRF spectrometer. Line separation of the characteristic x-rays of an element from those of its neighbours in the periodic table depends on resolving the spectral peaks. [5] Fig. (3.4) illustrates the high resolution performance of the spectrometer while measuring an x-rays. The Kα and Kβ peaks are separated by only 597 eV. The resolution expressed in Full Width at Half Maximum (FWHM) is measured and found to be 187 eV, using 5.89 KeV Kα x-ray of Fe-55 isotopic source.
FIG(3.3) Si(ll) Detector Diode
Fig(3.4) Mn X-Ray spectrum measured by a high resolution silicon detector spectrometer. Mn X-Rays from a Fe source.
3.4. **Signal Processing Electronics**

3.4.1. **Preampifier**

A charge \( Q \) released in the detector flows into an input circuit of a total capacitance \( C \) and produces a voltage signal \( Q/C \). (7) In dealing with these signal pulses from the radiation detector, it is often desirable to change the shape of the pulse in some predetermined fashion. By far, the most common application is in processing a train of pulses produced by the preamplifier. In order to assume that complete charge collection occurs, the preamplifier is normally adjusted to provide a decay time for the pulses which is quite long. Because it is the amplitude that carries the basic information, then the "pile-up" of the pulses in the tail of the preceding pulses which has not fully decayed to zero can be a serious problem. As the time spacing between the nuclear pulses is random, each pulse can be superimposed in a different residual tail and resulting amplitude is no longer a good measure of the charge \( Q \) for that event. The ideal solution is to shape the pulses in such a way so as to produce a pulse train in which all the tails have been eliminated, but the information carried by the maximum amplitude of the pulse has been preserved. (5).

So the first element in the signal processing chain is the preamplifier, which is provided as an interface between the detector and the pulse processing electronics that follows. The preampli-
ier is usually located as close as possible to the detector, to minimize the capacitive loading on the detector. [5]

3.4.2. Linear Amplifier:
The primary function of the amplifier is to amplify the signal received from the detector-preamplifier combination to a level (commonly -10v maximum) at which the latter circuit can perform accurate amplitude analysis. But an equally important function is to apply filters which suppress the extremely low and extremely high frequencies, where the signal to noise ratio is poorest. [7] In order to obtain an improved energy resolution, the voltage amplitude of the pulse at the amplifier output should be proportional to the detected x-ray photon energy.

The amplifier is also equipped with a pile-up rejection circuit, which is important in XRF work with its high count-rates.

3.4.3. Multi-Channel Analyzer (MCA):
The MCA here is used to measure the height of each amplifier output pulse and to represent this amplitude by an integral number. This is an Analogue-to-Digital Conversion (ADC) process. This digital information determines the memory address to which a count must be added. [7] The basic process used in all ADC's is to convert analogue input signal to an internally generated level which is
directly associated with a digital output generator.

The input gate on the ADC prevents signals entering
the system while an earlier one is being processed.
Finally a spectrum of the analysed signals is
obtained.

3.5. Data Analysis:

The analysis of x-ray spectra is carried out
using a computer program called Analysis of X-ray
Spectra by Iterative Least-Squares fitting (AXIL),
which is a Fortran program developed by Van Espan
for the deconvolution of complex x-ray spectra by
Si(Li) detector. The spectrum analysis is based on
non-linear least-squares fitting procedure optimiz-
ing the parameters of the fitting model (the param-
eters are obtained from energy and resolution
calibration, peak positions and intensities and
background .... etc). [6]

3.6. Sample and Sample Preparation:

The samples were supplied by the Blue Nile
Mines Company. They were mostly obtained from
Ingassena region. In any elemental analysis using
XRF, the process of sample preparation is still a
major difficulty. This is partly due to the fact
that only a thin layer of sample is used to perform
the elemental analysis. Also the sample must be
evenly distributed and homogeneously mixed for the
results to be representative of the whole sample.
An ideal sample for XRF would have the following characteristics: [9]

(i) Sufficient concentration of the elements of interest so that the elements could be detected.

(ii) Prepared in such a way that it is representative of the bulk material and at the same time with minimal sample preparation to avoid contamination.

(iii) Homogeneously mixed.

3.7. Sample Preparation for XRF:

The samples received were usually ground into fine powder at the Geology Department of the Ministry of Energy & Mining. They were then pressed into a pellet form using a pressing machine. The latter consists of die systems, comprising base cylinder, plunger, two pellets of steel and extraction ring. In fig. (3.5) is shown theSpecac pressing machine used in this work for making pellets.

The procedure for making a pellet is as follows:

The base is placed on the bench top, the cylinder is assembled onto the base and one of steel pellets is placed into the bore of the cylinder with polished face up. The sample is poured into the bore of cylinder and side of cylinder is tapped, so that the powder is homogeneously distributed across the face of the polished steel pellet. The second steel pellet is then inserted with polished face down. A
Fig. (3.5) The pressing machine setup.
pressure of about 15 tons is usually applied to make a good pallet. [10]

3.8. **Calibration of the tube-excited X-ray Spectrometer**

Measurements were performed to calibrate the tube-excited X-ray spectrometer using thick standards. Two secondary targets were used (Mo and Fe).

The X-ray generator, Siemens Kristalloflex 710K, was operated at 30 kV and 30 mA, in case of Fe secondary target, and 35 kV and 35 mA in case of Mo secondary target. The angle of incidence and emergence was 45.

3.8.1. **Theoretical Considerations**

In case of thick sample the intensity of the element can be expressed as:

$$I_i = \frac{S_i C_i}{\bar{\alpha}}$$  \hspace{1cm} 3.8-1

Where \(S_i\) is sensitivity of the XRF system (calibration constant), \(C_i\) is the concentration of the element \(i\) and \(\bar{\alpha}\) is average absorption which can be expressed as follows:

$$\bar{\alpha} = U(E_i) \sum C_i + U(E_i) \sum C_i$$  \hspace{1cm} 3.8-2

Where \(Q_i\) and \(Q_\alpha\) are the angles of incidence and emergence respectively, \(U(Q_i)\) and \(U(Q_\alpha)\) are mass attenuation coefficients for primary excitation photon of energy \(E_i\) and the fluorescent photon of
energy $E(i)$ respectively. In fig. (3.6) is shown the sample-secondary target-detector geometry.

The calibration of the XRF system is usually performed by measuring the fluorescent x-rays from thick single element standards and employing equation (3-8-1) to obtain for each element the calibration constant $k_i$. The average absorption $I$ for each sample of known composition is calculated using equation (3-8-2), and a computer program.

3.8.2. Measurements and Results:

The XRF Spectrometer consisted of PCT Si(Li) detector, Siemens X-ray tube excitation system, with secondary target geometry, together with Canberra electronics, including pile-up rejection. For light elements such as Al, Si, ... etc. Fe was used as secondary target. For medium and heavy elements, Mo was used secondary target. The anode material of X-ray tube was Mo. The spectral data were analyzed using Axios [11] program on Dec Professional 350 PC.

Sensitivities were prepared for K and L lines for the elements used. Some of the samples were pure elements in foil form while other samples were compounds in thick pallet form. The compounds were selected so there were no enhancement effects on the measured X-ray intensities.

In calculation of average absorption of primary and fluorescent x-rays within the thick standards, the total photo cross-section from the tables of Storm and Israel were used (available in computer...
Fig(3.6) Sample detector - secondary target geometry
The evaluated calibration constants $S$ for each element obtained from thick standards were quoted [in counts/sec/(gm-cm$^2$)].

The results obtained for each secondary target are tabulated in Tables (3.1) and (3.2). Graphs of sensitivity $S$ versus Z-number for each element are shown in Figs (3.7) and (3.8).
### Table: Sensitivity for X-ray Tube with OXTEC Detector

<table>
<thead>
<tr>
<th>Element</th>
<th>F (mA)</th>
<th>n (EI)</th>
<th>U (EI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.44kV</td>
<td>1.44kV</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2.75kV</td>
<td>2.75kV</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>3.32kV</td>
<td>3.32kV</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>3.72kV</td>
<td>3.72kV</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>4.86kV</td>
<td>4.86kV</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>5.95kV</td>
<td>5.95kV</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>6.35kV</td>
<td>6.35kV</td>
<td></td>
</tr>
</tbody>
</table>

**Fig (3.1):** Sensitivity for X-ray Tube with OXTEC Si(Li) detector. Fe Secondary Target.
<table>
<thead>
<tr>
<th>Z</th>
<th>2</th>
<th>E (keV)</th>
<th>I (fA)</th>
<th>I (fA)</th>
<th>$\Delta$ I</th>
<th>$\Delta$ I</th>
<th>m</th>
<th>$\Delta$ E (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>He</td>
<td>18.23</td>
<td>39.25</td>
<td>51.56</td>
<td>18.61</td>
<td>1.00</td>
<td>322.000</td>
<td>943.530</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>12.27</td>
<td>17.29</td>
<td>20.00</td>
<td>13.42</td>
<td>0.270</td>
<td>438.620</td>
<td>1131.710</td>
</tr>
<tr>
<td>13</td>
<td>Al</td>
<td>11.83</td>
<td>17.29</td>
<td>20.00</td>
<td>13.42</td>
<td>0.270</td>
<td>438.620</td>
<td>1131.710</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>11.83</td>
<td>17.29</td>
<td>20.00</td>
<td>13.42</td>
<td>0.270</td>
<td>438.620</td>
<td>1131.710</td>
</tr>
<tr>
<td>39</td>
<td>Y</td>
<td>14.84</td>
<td>22.88</td>
<td>25.65</td>
<td>18.40</td>
<td>0.670</td>
<td>2124.720</td>
<td>2450.840</td>
</tr>
<tr>
<td>50</td>
<td>Zr</td>
<td>15.74</td>
<td>22.88</td>
<td>25.65</td>
<td>18.40</td>
<td>0.670</td>
<td>2124.720</td>
<td>2450.840</td>
</tr>
<tr>
<td>Z</td>
<td>Sr</td>
<td>E [keV]</td>
<td>d [Fl]</td>
<td>u [Fl]</td>
<td>a1</td>
<td>c1</td>
<td>1 [sec]</td>
<td>8i [c/s/μg]</td>
</tr>
<tr>
<td>---</td>
<td>----</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
<td>----</td>
<td>----</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>34</td>
<td>W</td>
<td>9.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>Pt</td>
<td>8.43</td>
<td>129.666</td>
<td>129.404</td>
<td>358.345</td>
<td>1.0000</td>
<td>4273.555</td>
<td>1656.166</td>
</tr>
<tr>
<td>79</td>
<td>Au</td>
<td>9.70</td>
<td>124.612</td>
<td>129.165</td>
<td>358.291</td>
<td>1.0000</td>
<td>9214.688</td>
<td>1974680</td>
</tr>
<tr>
<td>80</td>
<td>Pb</td>
<td>9.84</td>
<td>127.514</td>
<td>116.008</td>
<td>358.247</td>
<td>1.0000</td>
<td>9252.080</td>
<td>1855370</td>
</tr>
<tr>
<td>82</td>
<td>U</td>
<td>13.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Values without intensity data were interpolated.
- Values with A are for K-alpha + K-peak.
- All K-series values are for K-alpha only.
- Values for L-series are for L-alpha only.
Fig (3.7): Variation of sensitivity with Z number.

Fe Secondary Target
4.1. Introduction:
Various authors have attempted to derive general mathematical relationships between the measured x-ray fluorescence intensity of an element and its concentration in a sample and the effect of other elements that might be present on the result either through absorption or through both absorption and enhancement.

We consider here a method introduced by Lachance-Trail that accounts for absorption by the matrix elements.

4.2. Lachance-Trail Method:

The basic relation for the intensity $I_i$ of element $i$ in a thick sample may be written as follows:

$$I_i = S_i \cdot C_i \cdot \frac{1}{\bar{a}} \quad (4.1)$$

where:
- $S_i$ = Sensitivity of element $i$ in sample
- $C_i$ = Concentration of element $i$ in sample
- $\bar{a}$ = average absorption in sample

The average absorption parameter $\bar{a}$ may also be written as:

$$\bar{a} = \sum_{j=1}^{N} \left( \frac{E_j \cdot E_i}{E_i} \right) C_j \quad (4.2)$$
i.e. as the sum of absorbance of \( E_1 \) and \( E_2 \) in all elements present.

Substituting (4.2) in (4.1) we get for the concentration of element \( i \):

\[
C_i = \frac{I_i}{C_i} \sum_{j=1}^{N} a_j (E_1, E_2) \cdot C_j
\]

We assume that:

\[
\sum_{j=1}^{N} C_j = 1
\]

Then taking \( C_i \) out of \( C_j \) in (4.3) we get:

\[
C_i = \frac{I_i}{C_i} \left[ a_i C_i + \sum_{j \neq i}^{N} a_j C_j \right]
\]

Also \( C_i \) can be written in form:

\[
C_i = 1 - \sum_{j \neq i}^{N} C_j
\]

Substituting (4.6) in (4.5) we get:

\[
C_i = \frac{I_i}{C_i} \left[ a_i + \sum_{j \neq i}^{N} (a_j - a_i) \cdot C_j \right]
\]

Generally equation (4.7) can be written in the Lechance-Trail form:

\[
C_i = \frac{I_i}{C_i} \left[ a_i + \sum_{j \neq i}^{N} \alpha_{ij} C_j \right]
\]

If there are two main elements in a sample e.g. Cr and Fe, then by applying equation (4.7) the concentrations of Cr and Fe in the sample may be written as:

\[
C_{Cr} = \frac{I_{Cr}}{C_{Cr}} \left[ a_{Cr} (E_1, E_{Cr}) + \sum_{j \neq Cr}^{N} (a_j (E_1, E_j) - a_{Cr} (E_1, E_{Cr})) \cdot C_j \right]
\]
and

\[ C = \frac{I_0}{C_0} \left[ a(E_1, E_0) + b(E_1, E_0) \right] \] (4.10)

We see that in equations (4.9) and (4.10) there are two unknowns \( C_{Cr} \) & \( C_{Fe} \) and four constants:

- \( a_{Cr} (E_1, E_0) \), \( a_{Fe} (E_1, E_0) \), \( a_{Cr} (E_1, E_0) \) and \( a_{Fe} (E_1, E_0) \). The quantities \( I_{Cr} \) and \( I_{Fe} \) are measured intensities and \( S_{Cr} \) and \( S_{Fe} \) are tabulated sensitivities. In order to determine the four constants we need to have two standards (of known concentrations) for the two elements Cr and Fe, for which the intensities \( I_{Cr} \) and \( I_{Fe} \) can be measured. Then from the four equations that can be written for the two elements in the two standards, similar to (4.9) and (4.10) values can be found for the four constants.

4.3. Use of Regression Method for Cr, Fe Analysis:

Since the sample is not made up of Cr and Fe only, we have to introduce an absorption factor to account for the matrix (other elements present in the sample besides Cr and Fe). Suppose Cr and Fe constitute the fraction \( K \) in the sample. The matrix elements present will then be \( 1-K \).

We can then introduce a correction factor for the matrix denoted by \( a_m \). Equations (4.9) and (4.10) then become:

\[ C = \frac{I_0}{C_0} \left[ a_m(E_1, E_0) + a(E_1, E_0) \right] \left[ a(E_1, E_0) - a_m(E_1, E_0) \right] \] (4.11)
\[ C_e = \frac{T_{fe}}{S_{re}} \left[ a_m (E_l, E_{fe}) a_v (E_e, E_{fe}) + \frac{1}{\alpha} (c_0, E_{fe}) \right] \quad (4.12) \]

Where:

1. \( a_m (E_l, E_{fe}) \) - average absorption in matrix of lines \( E_l \) & \( E_{fe} \).
2. \( a_v (E_e, E_{fe}) \) - average absorption in matrix of lines \( E_e \) & \( E_{fe} \).
3. \( a_v (E_l, E_{cv}) \) - average absorption in \( E_{cv} \) of standard for \( E_l \) & \( E_{fe} \).
4. \( a_v (E_l, E_{fe}) \) - average absorption in \( E_{fe} \) of standard for \( E_l \) & \( E_{fe} \).
5. \( a_v (E_e, E_{cv}) \) - average absorption in \( E_{cv} \) of standard for \( E_e \) & \( E_{fe} \).
6. \( a_v (E_e, E_{fe}) \) - average absorption in \( E_{fe} \) of standard for \( E_e \) & \( E_{fe} \).

The absorption factors 5, 4, 5 and 6 can easily be found using the computer program for:

\[ R = \text{CSCQ} \left[ U(E_l) + U(E_e) \right] \]

Where \( Q = 45^a \)

and \( E_{fe} = 17.4 \text{ keV} \) for Mo secondary target.

\( E_{fe} = 5.4 \text{ keV} \)

\( E_{cv} = 5.47 \text{ keV} \)

The constants determined using the two standards are then incorporated in the equations (4.11) and (4.12) for a sample (assuming a similar matrix for a sample and the standards). A computer program is then made for the determination of \( E_{cv} \) and \( E_{fe} \) in a sample, following the measurement of the intensities \( I_{cv} \) and \( I_{fe} \), and using the prepared sensitivities \( R_{cv} \) and \( S_{fe} \). (The program is given in Appendix II).
5.1. Introduction:

The samples that were selected for the measurements (as given in Table (5.1)) were suspected to contain the elements of interest such as Cr and Fe in group (1), Mn and Fe in group (2), Au in group (3), and light elements such as Al, Si in group (4), as described by the supplier, Blue Nile Mines. A comparative study was contemplated for the analysis of Cr and Fe between XRFPA and mathematical method (Regression method). The samples and standards were similarly prepared, for the analysis performed.

5.2. Measurements Using XRF:

For tube excitation system two secondary targets were used: Fe and Mo. In conjunction with PET Si(Li) detector spectrometer system. The former excitation source was intended to excite characteristic x-rays of the light elements, such as Al, Si and the latter excitation source for medium elements such as Cr, Mn, Fe and heavy elements such as Au. A bias supply of -1000 V was used for each Si(Li) detector. The amplifier settings were adjusted for optimum spectra for the elements of interest in each group together with pile-up rejection. As an example, usual settings applied on Canberra 2020 amplifier for excitation sources and spectrometer system used are shown in Table (5.2).
Table 5.1 List of geological samples supplied by Blue Nile Mines

<table>
<thead>
<tr>
<th>No. of Sample</th>
<th>group(1) samples</th>
<th>group(2) samples</th>
<th>group(3) samples</th>
<th>group(4) samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A62</td>
<td>Data 1</td>
<td>ST1</td>
<td>SR6P1</td>
</tr>
<tr>
<td>2</td>
<td>A56</td>
<td>Data 2</td>
<td>JCA</td>
<td>SR6P2</td>
</tr>
<tr>
<td>3</td>
<td>AH1</td>
<td>Data 3</td>
<td>JCA(1)</td>
<td>SR6P3</td>
</tr>
<tr>
<td>4</td>
<td>AU55</td>
<td>Data 4</td>
<td>JCI(2)</td>
<td>CC1/1</td>
</tr>
<tr>
<td>5</td>
<td>AB1</td>
<td>Data 5</td>
<td>CC2(2)</td>
<td>CC1/2</td>
</tr>
<tr>
<td>6</td>
<td>CC1</td>
<td>Data 6</td>
<td>CC2</td>
<td>T1</td>
</tr>
<tr>
<td>7</td>
<td>CC2</td>
<td>Data 7</td>
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<td>CCB1</td>
</tr>
<tr>
<td>8</td>
<td>Un 5/1</td>
<td>Data 8</td>
<td>CCB</td>
<td>CCB2</td>
</tr>
<tr>
<td>9</td>
<td>Q1</td>
<td>Data 9</td>
<td>CC1</td>
<td>CCC1</td>
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<td>Data 10</td>
<td>G1</td>
<td>CCC2</td>
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<td>12</td>
<td>Q8</td>
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<td></td>
</tr>
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<td>13</td>
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</tr>
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<td>15</td>
<td>x90</td>
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<td></td>
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</tr>
<tr>
<td>16</td>
<td>Conc(12)</td>
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</tr>
<tr>
<td>17</td>
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<tr>
<td>19</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>T1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>A 13/1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table (5.2)
Settings of Canberra Amplifier 2020 for the two secondary targets

<table>
<thead>
<tr>
<th>Target</th>
<th>Average energy (keV)</th>
<th>Bias supply (V)</th>
<th>Fine gain</th>
<th>Coarse gain</th>
<th>Sampling time (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>8.47</td>
<td>-1000</td>
<td>1.3</td>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td>Au</td>
<td>17.4</td>
<td>-1000</td>
<td>0.8</td>
<td>300</td>
<td>10</td>
</tr>
</tbody>
</table>

Table (5.3)
Concentration of the elements in standards

<table>
<thead>
<tr>
<th>Name of standard</th>
<th>Element</th>
<th>Concentration ($)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G005</td>
<td>CR</td>
<td>28.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>11.30</td>
<td></td>
</tr>
<tr>
<td>G305</td>
<td>CR</td>
<td>25.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>9.50</td>
<td></td>
</tr>
<tr>
<td>Mn ore</td>
<td>Mn</td>
<td>57.33</td>
<td></td>
</tr>
<tr>
<td>25C NBS</td>
<td>Fe</td>
<td>3.21</td>
<td></td>
</tr>
<tr>
<td>Al Si</td>
<td>Al</td>
<td>30.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>12.62</td>
<td></td>
</tr>
<tr>
<td>Gold ore</td>
<td>Au L</td>
<td>-</td>
<td>17.8</td>
</tr>
<tr>
<td>MA-1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The energy calibration for the system was carried out regularly before each measurement. This was usually done using Am-241 source. In Fig. (5.1) is shown a spectrum of Am-241 x-ray source.

The standards for groups 1, 2 and 3 samples were obtained from the Geological Department, Ministry of Energy & Mining. The standards for group 4 samples were prepared in the laboratory using oxides of the elements Al and Si.

Table (5.1) shows the concentration of the elements in standards. These standards were made into pellets in the same way as the samples.

For medium and heavy elements the samples and standards were measured using Mo as secondary target, and for the light elements Al and Si measurements were carried out using Fe as secondary target. All spectra were transferred to Dec Professional 350 PC Computer for analysis by Axil [11] Software. The Axil software is able to separate overlapping peaks, and in this way to identify the elements, using the library of elements, as well as to determine the net area of the peaks. A typical result obtained using Axil for one of the studied samples is shown in Fig (5.2). The QXRF Software also available at Dec Professional Computer, is then used for quantitative analysis of the samples, using the output files of the Axil for standards and samples. More detailed information on QXRF Software is given in Appendix (1).

The tube excitation system consisted of Siemens
Fig. 5.1: A typical spectrum of Am-241 source used for energy calibration.
Fig. 5.2  A typical results of analysis of sample using XRF obtained by AXIL program
Krystalloflex X-ray generator with Mo anode tube. The spectrometer system consisted of PUT Si(Li) detector coupled to Canberra 8-35 plus NCA via Canberra 2020 amplifier. A secondary target of Fe (having an average energy for Kα,β of 5.47 keV) was used for excitation of light elements Al & Si, while for medium and heavy elements such as Cr, Fe, Mn and Au a Mo secondary target (of average energy K of 17.4 keV) was used for excitation. Both standards and samples were measured under similar conditions and the spectral transferred to DEC Professional Computer for data analysis. The sample holder and secondary target holder are shown in Fig. (3.3). X-rays emitted by the Mo anode tube come out through one of the tube windows at 90° and strike the secondary target at 45°. Characteristic X-rays of secondary target that are emitted at 45° pass through Al collimator to strike the sample at 45°. Characteristic X-rays are emitted at 45° pass through Al collimator to the Si(Li) detector. Details of the Si(Li) detector dimensions are given in Fig. (3.3).
Chapter Six

RESULTS AND DISCUSSIONS

6.1. Results:

The first task of this analysis was to determine Cr & Fe concentration in soil and rock samples from Ingweanga area, using XRF. The soil samples varied in colour from reddish to black. The measurements were carried out using tube excitation technique, with No as secondary target. The concentrations were evaluated using the XRF methods: one based on QXRF software and the other on mathematical coefficients method (Regression Method). The idea was to be able to judge the various advantages and disadvantages encountered during the study of the two methods. Of course each of these methods could easily be used for quite satisfactory analysis of the given samples. However, it was decided to compare the two methods. More discussion and comparisons about the methods will be given later in the chapter.

The concentrations evaluated by using the QXRF technique (described in Appendix I) are given in Table 6.1. Twenty three (23) samples were analyzed by this method about eighty (80) samples.

Figs. (6.1) show some of the spectra fitted. The concentrations of Cr, Fe as measured by Regression method are shown in Table 6.2. The main sources of error in a measured concentration were estimated as follows:
\[ \text{Total error} = \sqrt{(\sigma_1^2 + (\sigma_2^2 + (\sigma_3^2 + (\sigma_4^2 + ... \ (6.1) \]}

Where:

- \( \sigma_i \) is the statistical error given by \( \sqrt{N/n} \times 100\% \)

where: \( N \) = counts per second

- \( \sigma_1 \) = Positioning of samples (about 0.5\%)
- \( \sigma_2 \) = Standard's error (about 1.0\%)
- \( \sigma_3 \) = Inter-element effects (absorption & enhancement) by matrix (about 1\%)

The XRF technique is also employed to investigate gold in soil and rock (e.g. marble, quartz) samples. The samples' color varied from bright yellow to brown. The concentrations were calculated using XRF technique. The results of measurement are tabulated in Table (6.3). Twenty (20) samples from matrix (60) samples were analyzed. Fig. (6.2) shows a typical result of analysis of gold sample using XRF, in conjunction with Azil software. Fig. (6.1) shows some of the spectra fitted for gold samples. The concentrations of these samples show small deviations from what might be expected. The reasons for this are discussed in a later chapter.

Tube excitation XRF showed difficulty in the analysis of Al and Si. This is due to air absorption problems, since Al-\( K \)-rays have only 1.5 KeV energy while Si 1.7 KeV energy. These energies would suffer greatly from matrix absorption as well as absorption in air. In the whole, one could say that the results for Al and Si which are tabulated in Table (6.4), give an idea about the presence of Al and Si. XRF has the advantage of quick identification of the
<table>
<thead>
<tr>
<th>ELEM</th>
<th>I, kg</th>
<th>A, cm²</th>
<th>CHAN</th>
<th>EWhn</th>
<th>AREA 1</th>
<th>STDEV1</th>
<th>CHI 1</th>
<th>TOTALS</th>
</tr>
</thead>
<tbody>
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<td>Ni</td>
<td>7.478</td>
<td>66.282</td>
<td>45.6</td>
<td>263.</td>
<td>1567.</td>
<td>286.</td>
<td>0.4</td>
<td>9.581E-04</td>
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<tr>
<td></td>
<td>7.461</td>
<td>66.216</td>
<td>45.5</td>
<td>263.</td>
<td>1567.</td>
<td>286.</td>
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<td>9.581E-04</td>
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<td></td>
<td>6.263</td>
<td>11.877</td>
<td>471.2</td>
<td>685.</td>
<td>1124.</td>
<td>72.</td>
<td>0.8</td>
<td>1.717E-08</td>
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<tr>
<td>Cu</td>
<td>8.040</td>
<td>58.212</td>
<td>458.9</td>
<td>265.</td>
<td>2263.</td>
<td>73.</td>
<td>0.6</td>
<td>1.139E-03</td>
</tr>
<tr>
<td></td>
<td>8.030</td>
<td>58.216</td>
<td>457.7</td>
<td>266.</td>
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<td>1.724E-03</td>
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<td>6.935</td>
<td>11.846</td>
<td>507.6</td>
<td>667.</td>
<td>571.</td>
<td>20.</td>
<td>1.0</td>
<td>1.459E-03</td>
</tr>
<tr>
<td>Zn</td>
<td>6.638</td>
<td>58.069</td>
<td>492.3</td>
<td>566.</td>
<td>2793.</td>
<td>69.</td>
<td>1.5</td>
<td>1.557E-03</td>
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<tr>
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<td>8.562</td>
<td>59.864</td>
<td>491.2</td>
<td>566.</td>
<td>2793.</td>
<td>51.</td>
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<td></td>
<td>9.572</td>
<td>17.042</td>
<td>545.6</td>
<td>660.</td>
<td>1531.</td>
<td>76.</td>
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<td>1.793E-03</td>
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<tr>
<td>Pb</td>
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<td>56.054</td>
<td>601.3</td>
<td>72.</td>
<td>3770.</td>
<td>370.</td>
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<td>2.187E-03</td>
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<td>10.402</td>
<td>6.375</td>
<td>595.6</td>
<td>77.</td>
<td>374.</td>
<td>34.</td>
<td>1.7</td>
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<td></td>
<td>12.403</td>
<td>11.667</td>
<td>716.7</td>
<td>77.</td>
<td>1732.</td>
<td>67.</td>
<td>4.4</td>
<td>3.510E-03</td>
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<tr>
<td></td>
<td>12.403</td>
<td>11.334</td>
<td>719.2</td>
<td>77.</td>
<td>1041.</td>
<td>40.</td>
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<td>3.542E-03</td>
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<td></td>
<td>14.704</td>
<td>4.053</td>
<td>641.0</td>
<td>183.</td>
<td>378.</td>
<td>15.</td>
<td>0.6</td>
<td>3.893E-03</td>
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<td>9.182</td>
<td>3.235</td>
<td>593.6</td>
<td>68.</td>
<td>142.</td>
<td>5.</td>
<td>1.4</td>
<td>1.667E-03</td>
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<td>Au</td>
<td>8.440</td>
<td>2.261</td>
<td>491.0</td>
<td>266.</td>
<td>9.</td>
<td>1.</td>
<td>1.3</td>
<td>1.270E-03</td>
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<td>9.712</td>
<td>43.177</td>
<td>503.4</td>
<td>269.</td>
<td>224.</td>
<td>40.</td>
<td>1.5</td>
<td>1.793E-03</td>
</tr>
<tr>
<td></td>
<td>11.446</td>
<td>52.661</td>
<td>651.9</td>
<td>274.</td>
<td>366.</td>
<td>69.</td>
<td>1.2</td>
<td>2.648E-03</td>
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<tr>
<td>IR</td>
<td>10.770</td>
<td>100.000</td>
<td>227.7</td>
<td>265.</td>
<td>457.</td>
<td>72.</td>
<td>2.3</td>
<td>1.521E-03</td>
</tr>
<tr>
<td></td>
<td>10.700</td>
<td>100.000</td>
<td>227.7</td>
<td>272.</td>
<td>315.</td>
<td>139.</td>
<td>2.0</td>
<td>2.506E-03</td>
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<tr>
<td>IR</td>
<td>12.000</td>
<td>100.000</td>
<td>249.7</td>
<td>275.</td>
<td>805.</td>
<td>84.</td>
<td>2.0</td>
<td>2.966E-03</td>
</tr>
</tbody>
</table>

Fig. 6.2 A typical result of analysis of gold
Sample obtained with AVIL program

50
Fig(6.3): Attenuated Au Sampl's spectral.
elements and is much simpler to handle compared to chemical analysis. For accurate results of Al and Si, with XRF more attention is needed to the various problems of matrix absorption as well as absorption in air. A vacuum chamber may be useful in this respect, to get rid of air absorption.

Alternatively, light elements such as Al and Si may be analyzed easily using the neutron generator, if available. Such measurements were considered here using the neutron generator of the Department of Physics. However, this could not be done due to breakdown in the electric cables feeding the machine.

The results for the elements Mn, Fe in some other samples using XRF are shown in Table (6.5). The soil samples varied in colour from reddish to black. The red colour indicates enrichment of Fe.
Table (6.1):
Concentrations of Cr & Fe by QXNF measurements

<table>
<thead>
<tr>
<th>Name of the Sample</th>
<th>Concentration (%) of Cr</th>
<th>Concentration (%) of Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A62</td>
<td>47.99 ± 2.41</td>
<td>13.66 ± 0.70</td>
</tr>
<tr>
<td>A59</td>
<td>47.59 ± 2.39</td>
<td>13.85 ± 0.70</td>
</tr>
<tr>
<td>AII</td>
<td>36.64 ± 1.68</td>
<td>11.12 ± 0.55</td>
</tr>
<tr>
<td>AIII</td>
<td>17.07 ± 0.88</td>
<td>13.76 ± 0.59</td>
</tr>
<tr>
<td>A61</td>
<td>53.48 ± 2.69</td>
<td>16.05 ± 0.75</td>
</tr>
<tr>
<td>CCI</td>
<td>0.30 ± 0.02</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>CCI/2</td>
<td>0.13 ± 0.01</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>A35/1</td>
<td>15.14 ± 0.76</td>
<td>12.10 ± 0.61</td>
</tr>
<tr>
<td>Q1</td>
<td>37.30 ± 1.91</td>
<td>19.20 ± 0.56</td>
</tr>
<tr>
<td>Q2</td>
<td>36.09 ± 1.81</td>
<td>20.20 ± 1.02</td>
</tr>
<tr>
<td>Q4</td>
<td>42.00 ± 2.11</td>
<td>20.07 ± 1.01</td>
</tr>
<tr>
<td>Q5</td>
<td>45.50 ± 2.34</td>
<td>21.10 ± 1.06</td>
</tr>
<tr>
<td>US1</td>
<td>25.90 ± 1.35</td>
<td>12.70 ± 0.62</td>
</tr>
<tr>
<td>US2</td>
<td>15.80 ± 0.65</td>
<td>13.50 ± 0.70</td>
</tr>
<tr>
<td>US3</td>
<td>31.50 ± 1.71</td>
<td>15.30 ± 0.77</td>
</tr>
<tr>
<td>R90</td>
<td>33.55 ± 2.01</td>
<td>10.77 ± 0.54</td>
</tr>
<tr>
<td>Conc1</td>
<td>29.13 ± 1.01</td>
<td>51.29 ± 2.58</td>
</tr>
<tr>
<td>Conc11</td>
<td>22.21 ± 1.12</td>
<td>45.01 ± 2.30</td>
</tr>
<tr>
<td>Conc111</td>
<td>26.22 ± 1.42</td>
<td>19.45 ± 0.58</td>
</tr>
<tr>
<td>CF</td>
<td>0.07 ± 0.01</td>
<td>8.95 ± 0.44</td>
</tr>
<tr>
<td>T1</td>
<td>41.67 ± 2.03</td>
<td>10.53 ± 0.33</td>
</tr>
<tr>
<td>A13/1</td>
<td>43.81 ± 2.20</td>
<td>11.62 ± 0.58</td>
</tr>
<tr>
<td>Name of the Sample</td>
<td>Concentration (%) of Cr</td>
<td>Concentration (%) of Fe</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>AS2</td>
<td>4.75 ± 2.37</td>
<td>12.59 ± 0.63</td>
</tr>
<tr>
<td>AS9</td>
<td>6.92 ± 2.35</td>
<td>12.57 ± 0.63</td>
</tr>
<tr>
<td>AH1</td>
<td>2.88 ± 1.83</td>
<td>10.04 ± 0.51</td>
</tr>
<tr>
<td>AUS5</td>
<td>17.13 ± 0.36</td>
<td>12.49 ± 0.63</td>
</tr>
<tr>
<td>AB1</td>
<td>52.59 ± 2.64</td>
<td>13.67 ± 0.69</td>
</tr>
<tr>
<td>OCI</td>
<td>0.25 ± 0.14</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>OCI</td>
<td>0.72 ± 0.00</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>US6/1</td>
<td>14.68 ± 0.75</td>
<td>10.98 ± 0.55</td>
</tr>
<tr>
<td>Q1</td>
<td>37.27 ± 1.87</td>
<td>17.43 ± 0.37</td>
</tr>
<tr>
<td>Q2</td>
<td>36.39 ± 1.63</td>
<td>18.34 ± 0.82</td>
</tr>
<tr>
<td>Q4</td>
<td>41.31 ± 2.08</td>
<td>18.22 ± 0.91</td>
</tr>
<tr>
<td>Q8</td>
<td>45.63 ± 2.30</td>
<td>19.16 ± 0.96</td>
</tr>
<tr>
<td>US1</td>
<td>26.46 ± 1.33</td>
<td>11.08 ± 0.56</td>
</tr>
<tr>
<td>US2</td>
<td>15.52 ± 0.33</td>
<td>12.62 ± 0.63</td>
</tr>
<tr>
<td>US3</td>
<td>33.44 ± 1.56</td>
<td>15.69 ± 0.70</td>
</tr>
<tr>
<td>ASO</td>
<td>39.33 ± 1.92</td>
<td>9.78 ± 1.96</td>
</tr>
<tr>
<td>Donor1</td>
<td>13.88 ± 0.99</td>
<td>46.57 ± 2.54</td>
</tr>
<tr>
<td>Donor11</td>
<td>21.84 ± 1.09</td>
<td>41.60 ± 2.09</td>
</tr>
<tr>
<td>ComC</td>
<td>27.05 ± 1.40</td>
<td>17.65 ± 0.89</td>
</tr>
<tr>
<td>GP</td>
<td>3.87 ± 0.03</td>
<td>8.09 ± 0.11</td>
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<tr>
<td>T11</td>
<td>43.98 ± 2.06</td>
<td>9.56 ± 0.48</td>
</tr>
<tr>
<td>A13/1</td>
<td>43.02 ± 2.17</td>
<td>10.55 ± 0.53</td>
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</table>
Table (6.4)

Concentration of Au by QXRF measurement

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<thead>
<tr>
<th>Name of the Sample</th>
<th>Concentration (PPm.) of Au</th>
</tr>
</thead>
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<tr>
<td>ST</td>
<td>17.8 ± 0.9</td>
</tr>
<tr>
<td>CC</td>
<td>13.1 ± 0.7</td>
</tr>
<tr>
<td>CC (1)</td>
<td>15.5 ± 0.8</td>
</tr>
<tr>
<td>CC (2)</td>
<td>12.1 ± 0.6</td>
</tr>
<tr>
<td>CC (3)</td>
<td>10.4 ± 0.5</td>
</tr>
<tr>
<td>CC (4)</td>
<td>0.6 ± 0.02</td>
</tr>
<tr>
<td>CC (5)</td>
<td>9.0 ± 0.5</td>
</tr>
<tr>
<td>CC (6)</td>
<td>7.4 ± 0.4</td>
</tr>
<tr>
<td>CC (7)</td>
<td>0.3 ± 0.01</td>
</tr>
<tr>
<td>GT</td>
<td>12.3 ± 0.6</td>
</tr>
<tr>
<td>PT</td>
<td>8.4 ± 0.4</td>
</tr>
<tr>
<td>CC North</td>
<td>9.8 ± 0.5</td>
</tr>
<tr>
<td>CAE</td>
<td>8.0 ± 0.4</td>
</tr>
<tr>
<td>AR</td>
<td>11.5 ± 0.5</td>
</tr>
<tr>
<td>CAM</td>
<td>8.8 ± 0.4</td>
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<tr>
<td>BL</td>
<td>15.4 ± 0.8</td>
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</table>
### Table (6.4)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (%)</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SREP 1</td>
<td>13.3 ± 0.7</td>
<td>5.4 ± 0.2</td>
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<tr>
<td>SREP 2</td>
<td>13.3 ± 0.7</td>
<td>25.1 ± 1.3</td>
</tr>
<tr>
<td>SREP 3</td>
<td>11.4 ± 0.6</td>
<td>27.5 ± 1.4</td>
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<tr>
<td>CC 1/1</td>
<td>11.8 ± 0.6</td>
<td>16.0 ± 0.8</td>
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<tr>
<td>CC 1/2</td>
<td>10.5 ± 0.5</td>
<td>21.5 ± 1.1</td>
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<tr>
<td>T1</td>
<td>20.9 ± 1.0</td>
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<tr>
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<td>18.7 ± 0.9</td>
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<tr>
<td>CC32</td>
<td>3.7 ± 0.2</td>
<td>30.2 ± 1.4</td>
</tr>
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<td>6.5 ± 0.3</td>
<td>27.7 ± 0.3</td>
</tr>
<tr>
<td>CC2</td>
<td>5.7 ± 0.3</td>
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### Table (6.5)

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<th>Concentration (%)</th>
</tr>
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<tbody>
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<td>Data 1</td>
<td>46.06 ± 2.42</td>
<td>1.49 ± 0.75</td>
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<td>Data 2</td>
<td>13.24 ± 0.67</td>
<td>5.56 ± 0.28</td>
</tr>
<tr>
<td>Data 3</td>
<td>45.46 ± 2.29</td>
<td>1.74 ± 0.05</td>
</tr>
<tr>
<td>Data 4</td>
<td>16.00 ± 0.80</td>
<td>6.41 ± 0.22</td>
</tr>
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<td>23.40 ± 1.17</td>
<td>3.12 ± 0.16</td>
</tr>
<tr>
<td>Data 6</td>
<td>18.51 ± 0.93</td>
<td>5.01 ± 0.25</td>
</tr>
<tr>
<td>Data 7</td>
<td>29.06 ± 1.06</td>
<td>6.51 ± 0.33</td>
</tr>
<tr>
<td>Data 8</td>
<td>37.81 ± 1.90</td>
<td>5.32 ± 0.12</td>
</tr>
<tr>
<td>Data 9</td>
<td>43.53 ± 2.04</td>
<td>3.53 ± 0.18</td>
</tr>
<tr>
<td>Data 10</td>
<td>41.27 ± 2.07</td>
<td>4.76 ± 0.21</td>
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</table>
6.2. Discussion:

1. Tube excitation consists of x-ray generator with tube head, and target anode, with special attachment for secondary target and sample holder. It requires cooling of the anode with cold clean water and therefore some time is needed to start the measurement. Since some time is required for the cooler to work till it reaches a certain temperature of about 10°C. Also some time is needed to warm up the machine. Also the target anode used in tube has a certain lifetime. There is no hazard placing a sample for measurement and removing it, since these can be done with the machine off. However, there can be a certain radiation hazard while the machine is running if no proper shielding is done. In the present system adequate shielding and precautions have been made. Irradiation time usually about 1000 seconds per sample for Cr, Mn, Fe, Al, Si samples, and about 4000 seconds per sample for Au samples. The important advantage of tube excitation as compared to isotopic source excitation is the high x-ray intensity. Unlike isotopic source, tube excitation x-rays do not suffer from decay and remain constant for a long time.

2. We observe during the measurements performed the poorer performance of tube excitation with regard to the analysis of Al and Si. Clearly
some problems exist with regard to Al and Si analysis. May be the longer distances travelled in air by the Al and Si X-rays (with energy only 1.5 keV for Al and 1.7 keV for Si) before they enter a Compton's striking absorption of the signals. This problem could be solved if a vacuum chamber is used for analysis of such low energy X-rays. Otherwise it would be advisable to analyze such elements by Neutron generator.

3. The main objective of this study was to establish a fast and accurate method for the analysis of Cr and Fe in chromite samples. Cr is one of the important minerals in Sudan and there is a great need to establish a fast method for its analysis. Two methods have been established for its analysis using XRF: one based on NBS software for analysis, and the other on use of mathematical methods for matrix absorption correction. The results obtained from the two methods are comparable. The mathematical method (also called Regression method) needs some initial preparations, such as sensitivity measurements, preparation of standards and computer program. Once this is done it is then very easy to analyze a sample. In the XRF based on NBS software there is also need to prepare a standard and then to run AsL program, followed by QRPF program. On the whole it appears that the Regression method is the faster one.
4. The analysis of Au in samples from South eastern Sudan was another objective of this study, with great demand in the market (Blue Nile Mines Company in particular was pressing for this). The analysis is not easy to do for the following reasons:

(i) The quantities required to determine are very small, only a few ppm or less, which is in the limit of detection by the XRF technique.

(ii) Au is not included in the library of the XRF program used for separation of overlapping peaks and determination of peak areas.

(iii) Au is not included also in the XRF WDS software (there is no data for its alpha coefficients, which account for matrix absorption corrections).

(iv) Au has several peaks in its L lines, with most of them appearing in a region of high Compton scattering from the tube excitation source, which makes it difficult to analyse it.

A lot of effort was devoted for the analysis of Au in this study. Eventually a method was established which gives reliable results. There is need for comparison with other methods for the analysis of Au which are not presently available.
5. The analysis of Mn and Fe does not constitute a big problem, since it is similar to the procedures adopted for the analysis of Cr and Fe. There is also great demand locally for its analysis. A reliable fast method has been established for its analysis using XRF software. Regression method can also be attempted.

6. Main sources of error in this measurement may include: homogeneity of the sample (about 0.5%), sample positioning during measurement (about 0.5%), absorption and enhancement by matrix (about 1%) and finally statistics (about 1% to 5%). All such errors are quadratically added and the final error is the square root of such sums (eqn. 5.1).
The use of XRF technique is receiving wide
spread attention on account of its ease and rapidity
for the analysis of a wide range of elements,
extending from Al (Z=13) up to U (Z=92). The
technique is able to determine major, minor and
trace element concentrations in various samples,
including geological, bio-medical, environmental and
other samples. It has become possible to perform
such analysis in a fast manner, with better
precision and accuracy.

In this work the XRF technique has been applied
for the elemental analysis of soil and rock samples
suspected to be rich in minerals such as Cr, Fe, Na
and Au. Attempts were also made to determine Al and
Si content in some of the samples. The samples were
supplied by Blue Nile Mines Company, which showed
great interest for the determination of the above
elements. From the work done and results obtained
one could make the following conclusions:

1. On the whole the XRF technique was used
   successfully for the determination of the
elements of interest: Cr, Fe, Na and Au. The
results were reliable and agreed well with
determinations that were performed
independently by the Geological Department,
Ministry of Energy & Mining, for some of the
samples that were used to check the technique.
2. Special attention was given to the analysis of Cr and Fe in chromate samples from Ingassana region, since this is the main mineral produced and exploited in this country. Two XRF methods were used for the analysis of the samples: one based on NBS (USA) software and the other on a mathematical (Regression) method that accounted for the matrix effects. Although the Regression method required some initial preparation work, such as sensitivity measurement and analysis of two standards in the end it proved to be comparable with the other method and slightly faster. All that would be needed for analysis of a sample is to prepare a pellet for it (about 15 min.) then perform the measurement (about 20 min.) and finally apply AXIL program and a Basic Program (about 5 min). The other method might take slightly longer time, with similar time for pellet making, measurement and AXIL program, but more time with QXRF program.

3. The analysis of Na and Fe is similar to Cr and Fe in its ease and rapidity. Similarly, one could easily prepare a Regression method for it.

4. The analysis of K4 presented some difficulty, since the concentrations looked for were in the trace element range (on the border of the detection limit of the XRF technique). This required longer time of measurement extending to more than an hour (4000 sec). The computer
analysis was not easy since Au was not present in the AXIL program library. It was necessary to prepare a library for it after measurement of a pure Au sample to determine the main peaks and intensities. The QAXF software also lacked alpha coefficient data, necessary for matrix absorption correction. However, with careful fitting of the spectra of the standard and samples it was possible to obtain reliable results.

5. The analysis of Al and Si presented some difficulty since these two elements are on the lower energy limit of the XRF technique. The low energies of Al (1.5 keV) and Si (1.7 keV) suffered from absorption in the air during their passage from the sample to the Be window of the Si(Li). Further absorption would occur in the sample itself and the Be window. To overcome such difficulty it would be advisable to shorten the sample - detector distance, and to work in a vacuum chamber. Otherwise it would be better to attempt measurement by fast Neutron Activation Analysis with the Neutron generator, available in the Department of Physics.

6. The precision of the measurements using the XRF technique is estimated to be on average about 5%. The results are assumed to be highly reliable. The analysis is non-destructive, easy to perform and fast.
APPENDIX I

INSTRUCTIONS FOR OPERATION AND USE OF THE QUANTITATIVE X-RAY ANALYSIS SOFTWARE (AXILNBS)

INTRODUCTION:

The AXILNBS software was developed to permit the user easy and direct communication between the AXIL Spectra Evaluation Program, and the NB SB SC FORTRAN Program for Quantitative X-ray Fluorescence Analysis. The AXILNBS transforms the output files of the AXIL in the form acceptable for the NB SB SC: the user has no need to type the values for the net areas into the NB SB SC programs. It is expected that this will not only ease the manipulation of the program but will also avoid the unnecessary mistakes introduced by reading and typing the data.

The user is advised to study the manuals for operation of the AXIL and NB SB SC programs. The first one can be obtained by contacting the IAEA, Physics Section, the second from National Bureau of Standards, Center for Analytical Chemistry, Gaithersburg, Maryland 20899, USA. The AXILNBS program has been developed for the use with DEC Professional series of desk computers. The sources for both programs are available in the IAEA, and can be obtained on request.
INSTALLATION OF AXIMMS:

The programme AXIMMS found on the diskettes is installed in the established manner, preferably into the same application group as the AXII programmes.

It is recommended to create a Directory called TRS. (in fact, the files of AXIMMS can be put in any other directory, but having them all in the Directory TRS will considerably simplify the operation. It will not be required to specify the directory with the needed file-(XXX)- every time that the file will be used). After creating the TRS file, copy into this directory the files found on the diskette in the Directory USERFILES. Volume XRAY. These are the files:

DIR0.DIR
DIR1.DIR
DIR2.DIR
DIR3.DIR
MOST.SOU
Pest.SOU
SDX75.SOU

The last three files specify the required input for calculation of alpha coefficients, in case that the Most and Pest are secondary target for the NHS X-ray tube excitation are being used. Other sources, or tube excited systems will require additional files.

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SPECIFICATIONS FOR AXIL:

The use of AXIL can proceed in the known fashion. The spectra are transferred from the RGA to the DEC Professional, with each spectrum receiving a name number of six digits (say 000555)

The spectrum is then analyzed using the input data as shown below:

<table>
<thead>
<tr>
<th>AXIL VERSION</th>
<th>LISA DEVICE</th>
<th>SPEC/CTRL</th>
<th>MAIN OUTPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>04</td>
<td>SYG:</td>
<td>CTRL:</td>
<td>SYG: ALLOYOS.DAT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SPEC/CTRL</td>
<td>TIT:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>INPUT FROM</td>
<td>0555,22,GREEN ALLOY 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the above example, the INPUT FROM specifies a file in the current directory which was obtained by improving the input data for calibration background, absorption and specified elements for the type of sample and the measuring setup used in the experiment.

The MAIN OUTPUT specifies that a file with the results of the AXIL calculations will be created on the DEC Professional (hard disk) and will be named ALLOYOS.DAT. This file will not be used later for transforming the format into the acceptable by the SMESS programme.

The SPEC/CTRL, CTRL, TIT is the usual prompt of the AXIL. In the example, the spectrum 000555 will be analyzed, the results will be written in the format specified by 22 (see AXIL manual). The name
of the results, CREFIN ALLOY 5, is important for the programme and contains data format acceptable by the NBSGSE programme.

After the analysis of the spectrum was completed and the file was prepared, you must exit AXIL by typing "STOP", before starting to analyze the next spectrum. Obviously, the next standard spectrum will have another name, say ALLOY02.DAT.

**USING THE QUANTITATIVE X-RAY FLUORESCENCE ANALYSIS SYSTEM**

After selecting this programme from the AXIL-MAIN main menu, the following secondary menu will appear:

```
1 Standard Sample File
2 Unknown Concentration Sample File
3 Alpha Coefficients File
4 Display Save Files
5 Delete a standard sample save file
6 Delete an unknown sample save file
7 Delete an alpha coefficients file
8 Sample concentration calculation
9 Exit
```

The files under 1, 2 and 3 will be created using the results of AXIL as found in the output AXIL file (in previous example: ALLOY01.DAT). It is advisable to start with the "Standard Sample File"

- **STANDARD SAMPLE FILE:**

Select 1 from the Menu. The first prompt is

```
INPUT FILE NAME: 
```

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and requires that the AXIL output file is specified ALLOY01, for example. After typing in the name of the file, and pressing RETURN, the screen will show: first, the original AXIL output file, second, the reformatted file that will serve as the input to quantitative analysis program.

The names of the elements in the sample will appear, with the energies and intensities (net areas). You will be prompted to contribute the concentration, as known from the certificate for the standard reference material (or from your own measurements, in cases when you prepared the reference materials yourself).

Finally, the program prompts you for a name for the newly created files:

```
[------------------------]
STANDARD FILE NAME:
[------------------------]
```

Insert any name but preferable different from the INPUT FILE NAME. For example, if the standards are alloys, one can use ALYSIS (standing for Alloy Standards number 5) for the sample which has the spectrum called 005505, and the AXIL output file called ALLOY05.

b. UNKNOWN CONCENTRATION SAMPLE FILE:

Select 2 from the Menu.

The prompt

```
[------------------------]
INPUT FILE NAME:
[------------------------]
```

will be answered by typing the AXIL output file name, say ALLOY05. If you have already prepared
the Standard Save Files, the programme will give you a choice of these files by displaying:

The following standard reference files available:
1 UNRGT
2 MfPeSIE
3 etc.
Which one do you want (1-9, D=NONE)

This is a convenience for the user. By selecting a standard file that has the same
analogies as in the unknown sample, the need to specify these elements by typing them in, is
avoided. The programme will select the proper elements by itself. However, if you select the
default value NONE (D is abbreviation for DEFAULT), you will have to input the elements using the
keyboard.

The programme will then ask you to give the file of the unknown sample a new name by:

SAMPLE FILE NAME

Again, you are free to specify any name. For example the UNKN.DAT will do the job. You can even
call the DAT part; the computer will add it by itself.

c. ALPHA COEFFICIENTS SAVE FILES

Select 3 from the Menu.

After display of date and time, the list of the Standard Save files will be shown. The programme prompts you by:

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6. DISPLAYING AND DELETING THE FILES:

The operation for deleting and displaying the standard, unknown, and alpha files are self-explanatory.

NOTE:

The numbers in the file DIR0 must be identical to the number of files in the directories DIR1, DIR2, and DIR3, otherwise the programme will not function. If the display of the DIR0 shows 6 2 1

There must be six standard files, two unknown, and one alpha file in the respective DIRS.

e. SAMPLE CONCENTRATION CALCULATION:

After all the files have been prepared, select 8.

Respond to the computer prompts by selecting one or more standard files, one or more unknown files, and one alpha coefficients file.
Select the appropriate fitting curve. In case of having only one standard, you will find out that you have no choice anyway.

If you did not make a mistake admire the excellent results.
THE COMPUTER PROGRAM:

A computer program is then made for determining the concentration of Cr and Fe in a sample, following the measurement of intensities per second for Cr and Fe as \( I_{Cr} \) and \( I_{Fe} \), and using the prepared sensitivities for Cr and Fe as \( S_{Cr} \) and \( S_{Fe} \).

The program is given as:

10: Mesa
15: Print: Print
20: Print "Chromate Concentration"
25: Print: Print
30: Input "Intensity of Cr(Kα + Kβ) ="; \( I_{Cr} \)
35: Input "Intensity of Fe(Kα) ="; \( I_{Fe} \)
40: Print: Print
45: \( D = \left( \frac{36549.25}{I_{Fe}} \right) \times \left( \frac{54035.5}{I_{Cr}} \right) - (38.95 \times 379.12) \)
50: \( C_{Cr} = \left( \frac{5168.89 \times (54035.5/ I_{Cr}) - (319.28 \times 39.95)}{D} \right) \)
55: \( C_{Fe} = \left( \frac{36549.25}{I_{Fe}} \right) \times \left( \frac{319.28 + 379.12}{5168.89/D} \right) \)
60: Print "Concentration (Cr) ="; \( C_{Cr} \)
65: Print "Concentration (Fe) ="; \( C_{Fe} \)
REFERENCES


