# Analysis of stainless steel samples by energy dispersive X-ray fluorescence (EDXRF) spectrometry

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**Abstract.** A simple method for the analysis of stainless steel samples is presented which is based on radioisotope excited energy dispersive X-ray fluorescence (EDXRF) spectrometry and does not require any type-standards. Both absorption and enhancement effects have been taken into account in the fundamental parameter method for quantitative analysis and an iterative approach is followed for calculation of concentrations in steel samples. Non-linear least square fitting (NL-LSF) procedures have been used to determine accurately the fluorescent peak intensities. The method has been tested by analysing several CRM standard reference samples and 304 and 316 steel samples assuming as unknown. The EDXRF results have also been compared with the results of analysis of same samples by vacuum emission spark spectrometry (VES). Obtained values for concentration in steel samples match quite well with their certified values.

**Keywords.** XRF; spectrometry; least squares fitting; stainless steel.

## 1. Introduction

Energy dispersive X-ray fluorescence (EDXRF) technique has become a powerful technique for non-destructive multielement analysis of materials. Over the last years, several developments have taken place in the methodology for quantitative analysis using this technique with the aim, on the one hand, to enhance the quality and reliability of the results, and to extend the range of its applications on the other hand. With the use of empirical and semi empirical algorithms (Lachance and Traill 1966; Claisse and Quintin 1967; Rasberry and Heinrich 1974), the elemental composition of the sample is determined by measuring the relative intensities of the X-ray fluorescent peaks with that of a set of multielement standards or pure elements. The comparative standards are desirable to be similar in shape, form and concentration to the unknown sample that sometimes limits the application of EDXRF due to the non-availability of such standards. The fundamental parameter method (FP) using iterative approach is a fast method (Sparks 1975; Sawhney and Lodha 1989) which can work even when type-standards are not available. This method gives reliable results for both trace and major element analysis provided the absorption and enhancement by the sample matrix is accounted for properly (Van Dyck *et al* 1986). The analysis of multi-component alloys like stainless steel (SS), in which both trace and bulk elements are required to be determined, is

some what complex as not only the matrix absorption-enhancement effects have to be corrected, but accurate peak intensities have to be determined from the complex spectra using some fitting procedures. Generally in stainless steel (SS) samples Ti(0·03–0·08), Si(0·03–1·1), C(0·03–0·06), P(0·005–0·035), S(0·005–0·012), W(0·02–0·3%) etc are present as minor components while Cr(3·2–24·4), Ni(3·7–21·5), Fe(50·0–70·0), Cu(0·6–2·2) and Mo(1·5–4·0%) are present as major components. Barrea and Mainardi (1998) have analysed the stainless steel samples by measuring two fluorescence spectra of same sample under two different excitation conditions, which provides a system of non-linear equations. Because two measurements are required to be done for each sample, the analysis time gets doubled in this method and moreover this method cannot be used in radioisotope excited XRF where the excitation energy is quasi-monochromatic. They could determine elements Cr, Fe, Ni, Nb, Mo only. They could not determine the concentration of minor elements like Mn, Co, Cu etc whose $K_a$ peaks strongly overlapped with the neighbouring major peaks.

In the present paper, we present a method for stainless steel analysis which is simple, fast, non-destructive and does not require any type-standards. We have determined elements Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo etc in the stainless steel samples. The quantitative analysis has been performed by our in-house developed CATXRF program (Tiwari and Sawhney 2000), which is based on FP method and corrects for both absorption and enhancement effects. The peak areas have been determined by the use of non-

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linear least square fitting (NL-LSF) procedures. Only one single element standard has been used for the determination of system geometry factor. To verify the method, it has been applied for the analysis of several certified reference materials (CRM) and SS-304 and SS-316 samples and the results obtained from our method have also been compared with the analytical results obtained by the analysis of same samples by vacuum spark emission spectrometry (VES).

## 2. Theory

For monochromatic excitation, the measured X-ray fluorescence intensity, $I_j$, is related to the analyte mass, $m_j$, by (Sparks 1975)

$$(I_j)_k = I_0 G \cdot K_j \cdot A \cdot m_j \cdot (1 + H_{jk}), \qquad (1)$$

where $K_j$ is the relative efficiency to excite and detect the fluorescent X-rays from element $j$ and is given by

$$K_j = t \left\{ 1 - \frac{1}{J_{K,L}} \right\} \cdot w_k \cdot e \cdot T \cdot f, \qquad (1a)$$

$A$ is the mass absorption correction factor and for infinitely thick samples, in which domain the stainless steel samples fall, is given by

$$A = \frac{1}{[m(E_0)\cos ec(\psi_1) + m(E_j)\cos ec(\psi_2)]}, \qquad (1b)$$

$H_{jk}$ is the enhancement factor and its value is zero for elements that are not enhanced by any other sample constituent. $H_{jk}$ for infinitely thick samples is given by Sparks (1975) as

$$H_{jk} = \frac{1}{2t_i(E_0)} \sum_{k=1}^{m} W_k \cdot w_k \cdot \left( 1 - \frac{1}{J_{kl}} \right) \cdot m_j(E_k) \cdot m_k(E_0)$$

$$\cdot \left[ \frac{\log\left(1 + \frac{m(E_0)}{m(E_k)\cdot\sin j_1}\right)}{\frac{m(E_0)}{\sin j_1}} + \frac{\log\left(1 + \frac{m(E_j)}{m(E_k)\cdot\sin j_2}\right)}{\frac{m(E_j)}{\sin j_2}} \right], \qquad (1c)$$

where $j, k$ = index of the analyte and enhancing element; $E_0$, $E_j$, and $E_k$ are the energies of primary radiation and characteristic energies of the $j$th and $k$th elements, $\Psi_1$, $\Psi_2$ represent entrance and exit angles, $G_0$ a geometrical factor, $I_0$ the intensity of primary radiation, $e$ the detector efficiency at the fluorescent energy $E_j$, $t$ the photoelectric mass absorption coefficient at primary energy, $J_{K,L}$ the jump ratio for the appropriate ($K$ or $L$) absorption edge, $T$ the transmission coefficient of the fluorescent X-rays in the air path, $f$ the fractional intensity of the X-ray line used for analysis, e.g $K_a/(K_a + K_b)$. $m(E_0)$, $m(E_j)$, $m(E_k)$ are the total sample mass absorption coefficients for X-ray

energies $E_0$, $E_j$ and $E_k$ respectively, $W_k$ is the weight fraction of the $k$th element, and $M$ is mass of sample in g/cm$^2$.

## 3. Experimental

Several CRM stainless steel samples and unknown samples were analysed on our EDXRF spectrometer (Sawhney *et al* 1998) consisting of a Si(Li) detector having an energy resolution of 155 eV at 5·9 keV. A 20 mCi Cd$^{109}$ annular radioisotope was used as an excitation source. The experimental setup is shown schematically in figure 1. A 3 mm thick aluminum mask having a centred hole of diameter 24·7 mm was used to ensure same illuminated surface area for all the samples. The sample-detector and excitation source-sample distances were optimized to get maximum count rate in the fluorescent peaks. Each sample was analysed for 1000 sec. The EDXRF spectra of SS samples are quite complex because of the presence of several small peaks from minor elements occurring near the big peaks of major elements and a simple deconvolution procedure cannot be used to derive the peak areas of such small peaks. Examples of such strong peak overlapping are the pairs of spectral lines Mn $K_a$–Cr $K_b$, Co $K_\alpha$–Fe $K_b$ and Cu $K_a$–Ni $K_b$. Therefore to derive accurate peak areas of such strongly overlapped peaks, we have used non-linear least square fitting method using ORIGIN software (Microcal Origin USA, 1995, Technical Graphics and Data Analysis Software). Two typical fluorescence spectra of T-216 and SS-304 samples are shown in figures 2 and 3. The system geometrical factor $I_0 G$ was determined by analysing a single element synthetic standard. To confirm the value of $I_0 G$, a few more synthetic standards of different elements in various
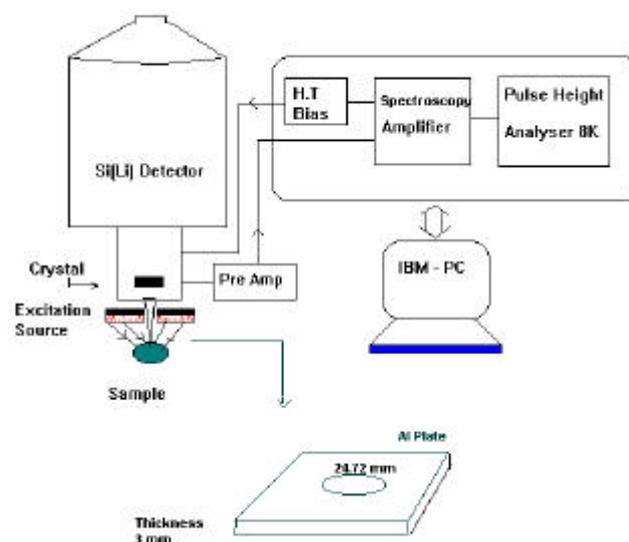


**Figure 1.** Schematic diagram of the experimental setup.

concentrations were prepared and analysed and $I_0G$ was found to be reproducible within ± 2%. All synthetic standards were prepared as pellets of diameter 24·7 mm from appropriate oxides. Quantitative analysis of all the SS samples was performed by the computer program CATXRF which is based on FP method and uses an iterative procedure to calculate the concentration of various elements present in the specimen. This program is written in FORTRAN-77 and runs on Pentium PCs. Details of the program are given elsewhere (Tiwari and Sawhney 2000). We have detected almost all the elements with $Z > 17$ present in steel samples, and the combined concentration of all other elements (C, P, Si, S etc) which cannot be detected by EDXRF spectrometry, is less than 1%. Hence no significant error is introduced in the elemental analysis if the presence of these low-Z elements

is ignored. Accordingly it is assumed in our EDXRF quantitative analysis that the total concentration of all elements detected by EDXRF is 100%. In the iterative procedure in CATXRF program, for the starting values, the specimen was assumed to comprise of Fe and cellulose in 1 : 1 ratio and the iteration was stopped when total concentration of all detected elements became 100%. The values of various fundamental parameters were taken from published literature (McMaster *et al* 1969; Bambynek *et al* 1972).

## 4. Results and discussion

Figure 2a shows a typical fluorescence spectrum of a T-216 reference sample obtained with EDXRF spectro-



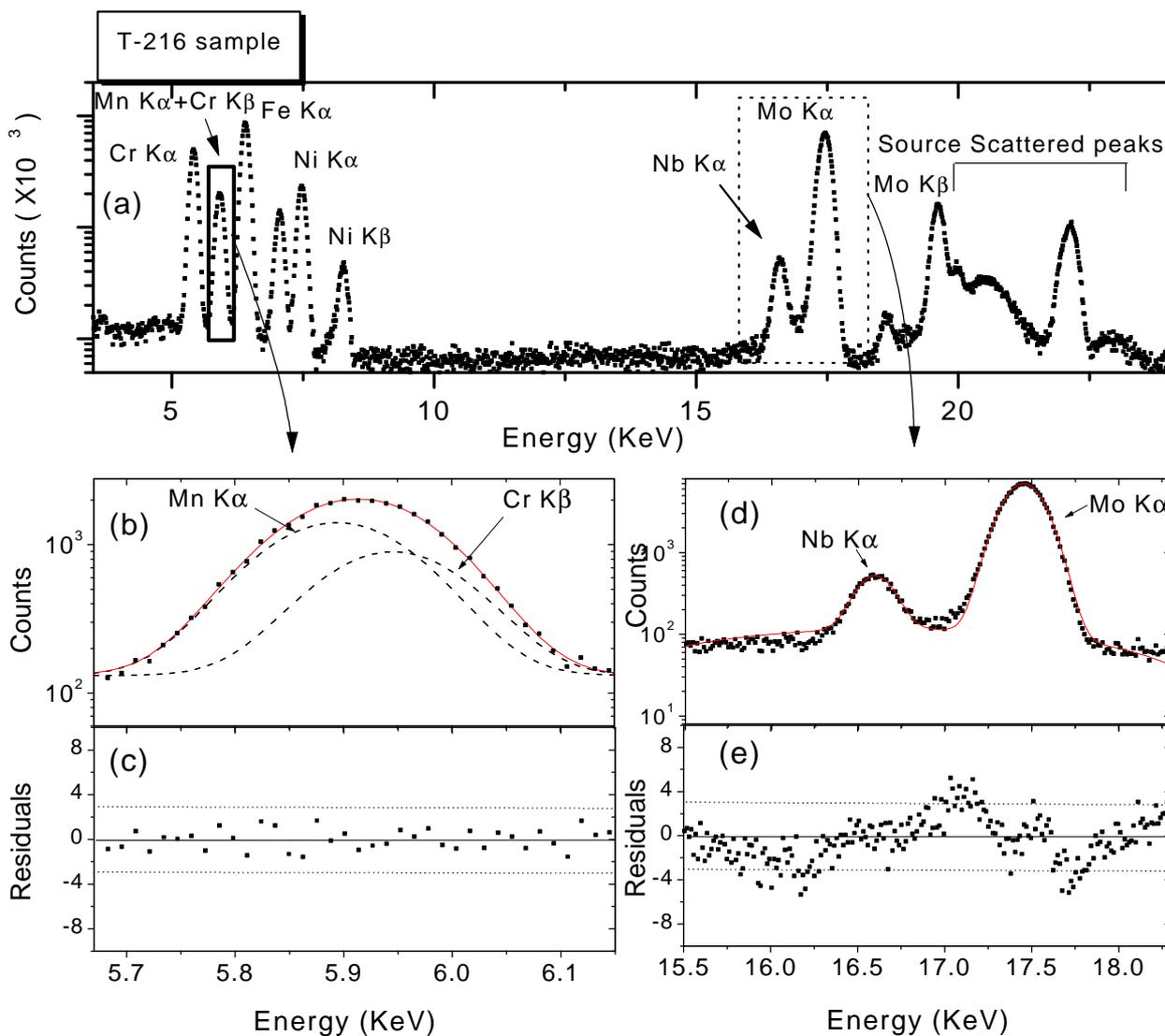**Figure 2.** (**a**) A typical EDXRF spectra of T-216 SS-reference sample, (**b**) merged Mn–$K_a$ and Cr–$K_b$ X-ray peaks fitted using NL-LSF procedures, (**c**) residuals of the fit in (**b**) in units of one standard deviation ($s = \sqrt{N}$, where $N$ is the counts accumulated in a given energy channel) of data; similarly (**d**) and (**e**) show fitting results obtained for Nb–Mo pair.
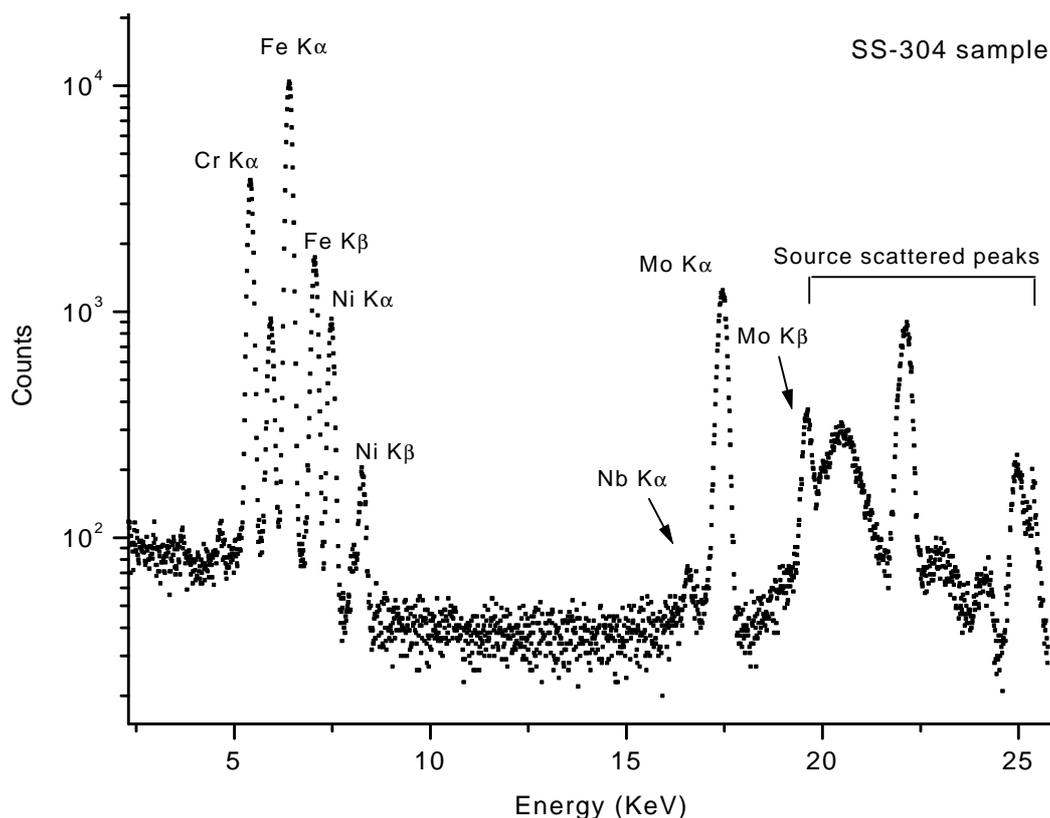
**Figure 3.** A typical EDXRF spectra of SS-304 sample.

meter. It is evident from the figure that the spectrum is quite complex with several peaks strongly overlapping. Owing to the complexity of the SS spectrum, the least squares fitting was done by dividing the spectrum into several regions. For instance figure 2b shows the Cr–Mn part of the spectrum for which the individual peak areas could only be derived by the use of NL-LSF procedure. The goodness of the fit is evident from figure 2c where the residuals of the fit are seen to fall within the ± 3$s$ limit (Van Grieken and Markowicz 1993). Similarly the fitting results obtained for the Nb–Mo part are shown in figures 2d and e. The Nb–Mo peaks fall on the tail of the broad Compton scattered source peak and hence the least squares fitting is not that perfect in this region which is reflected in relatively higher fitting residuals (figure 2e). Barrea and Mainardi (1998) could not determine the concentrations of minor elements like Mn, Co, Cu, Nb, etc because of strong overlaps and also non-correction of this type of overlaps ($K_b$ line of one element merging in $K_a$ intensity of another element) results in greater error in their analysis. On the other hand we have been able to determine accurately the concentrations of all elements detectable by EDXRF technique.

The concentrations of minor and major elements in various SS samples analysed by EDXRF technique are given in tables 1 and 2. Tables show that the concentration of all elements in each sample matches quite well

with their certified values. The overall relative analysis error range from 2% to 10%, which include errors contributed by geometrical reproducibility, counting statistics, errors in fundamental constants etc. The dominant error is the statistical error in the peak intensity determination which is higher for elements present in lower concentration. Various SS samples analysed by EDXRF technique were also analysed by VES (Vacuum Emission Spark Spectrometer, Model JY56E, Jobin Yvon, France). VES is an instrumental technique which is used in the elemental analysis of SS types of samples. The results of this analysis are also given in tables 1 and 2. These tables show that the EDXRF results are similar to VES results and in many cases the EDXRF results match with certified values better than VES results. VES technique is a destructive technique as it creates a spark spot on the sample surface and also requires several type-standards similar in concentration and form of the unknown samples for the calibration of the spectrometer. On the other hand, the method reported here based on EDXRF technique does not require any type-standards and is applicable for all types of steel samples. The main advantage of VES technique is that it also gives the concentrations of low Z elements like C, P, Si etc which are not detectable by EDXRF measurements. For most of the routine analysis of SS the analysis can be performed by EDXRF, which is

**Table 1.** Concentrations of CRM samples determined by EDXRF and VES.

| Sample no. | Elements | Concentrations (%) | | |
|---|---|---|---|---|
| | | Certified | By EDXRF | By VES |
| T-211 | Cr | 19·50 | 19·1 ± 0·40 | 18·4 ± 0·30 |
| | Mn | 1·80 | 1·84 ± 0·08 | 1·60 ± 0·05 |
| | Fe | 69·56 | 69·9 ± 1·60 | 69·9 ± 1·00 |
| | Ni | 8·61 | 8·4 ± 0·20 | 8·6 ± 0·10 |
| | Cu | 0·20 | 1381 ± 50   ppm | – |
| | Mo | 0·20 | 0·21 ± 0·02 | – |
| T-212 | Cr | 21·80 | 21·4 ± 0·50 | 21·4 ± 0·30 |
| | Mn | 0·83 | 0·9 ± 0·05 | 0·77 ± 0·02 |
| | Fe | 65·40 | 65·1 ± 1·50 | 67·6 ± 1·00 |
| | Co | 0·18 | 1630 ± 150 ppm | – |
| | Ni | 7·12 | 7·1 ± 0·20 | 6·5 ± 0·10 |
| | Cu | 1·37 | 1·36 ± 0·05 | – |
| | Nb | 0·01 | 192 ± 18   ppm | – |
| | Mo | 2·50 | 2·5 ± 0·05 | 2·3 ± 0·05 |
| T-213 | Cr | 21·60 | 22·0 ± 0·50 | 21·6 ± 0·33 |
| | Mn | 1·07 | 1·0 ± 0·05 | 1·0 ± 0·03 |
| | Fe | 64·90 | 65·2 ± 1·50 | 67·3 ± 1·00 |
| | Co | 0·26 | 0·4 ± 0·04 | – |
| | Ni | 7·24 | 7·2 ± 0·20 | 6·2 ± 0·10 |
| | Cu | 1·50 | 1·5 ± 0·05 | – |
| | Nb | 0·03 | 417 ± 40   ppm | – |
| | Mo | 2·53 | 2·56 ± 0·06 | 2·37 ± 0·05 |
| T-214 | Cr | 20·12 | 20·0 ± 0·40 | 20·3 ± 0·30 |
| | Mn | 1·45 | 1·49 ± 0·06 | 1·43 ± 0·04 |
| | Fe | 47·80 | 47·9 ± 1·10 | 48·6 ± 0·70 |
| | Co | 0·29 | 0·37 ± 0·03 | – |
| | Ni | 24·44 | 23·9 ± 0·60 | 23·9 ± 0·40 |
| | Cu | 1·42 | 1·49 ± 0·05 | – |
| | Nb | 0·01 | 226 ± 21   ppm | – |
| | Mo | 4·24 | 4·28 ± 0·09 | 4·53 ± 0·10 |
| T-215 | Cr | 18·63 | 19·4 ± 0·40 | 18·7 ± 0·28 |
| | Mn | 1·38 | 1·4 ± 0·06 | 1·50 ± 0·05 |
| | Fe | 65·40 | 65·0 ± 1·50 | 65·7 ± 1·00 |
| | Co | 0·01 | 1451 ± 133 ppm | – |
| | Ni | 10·95 | 10·9 ± 0·30 | 10·6 ± 0·20 |
| | Cu | 0·02 | 495 ± 18·0 ppm | – |
| | Nb | 0·76 | 0·81 ± 0·07 | – |
| | Mo | 2·20 | 2·3 ± 0·05 | 2·16 ± 0·04 |
| T-216 | Cr | 23·40 | 23·0 ± 0·53 | 23·6 ± 0·35 |
| | Mn | 5·60 | 5·8 ± 0·25 | 5·6 ± 0·14 |
| | Fe | 50·76 | 50·3 ± 1·10 | 50·9 ± 0·70 |
| | Co | 0·16 | 0·25 ± 0·02 | – |
| | Ni | 16·30 | 16·7 ± 0·40 | 15·2 ± 0·20 |
| | Cu | 0·15 | 0·21 ± 0·01 | – |
| | Nb | 0·24 | 0·24 ± 0·02 | – |
| | Mo | 2·92 | 3·0 ± 0·10 | 2·9 ± 0·06 |
| CRM-474 | Cr | 19·06 | 19·8 ± 0·45 | 18·7 ± 0·28 |
| | Mn | 1·70 | 1·68 ± 0·07 | 1·71 ± 0·04 |
| | Fe | 60·05 | 59·5 ± 1·40 | 60·5 ± 1·00 |
| | Ni | 14·70 | 14·8 ± 0·40 | 15·1 ± 0·30 |
| | Cu | 0·35 | 0·35 ± 0·01 | – |
| | Nb | 0·01 | 157 ± 14·0 ppm | – |
| | Mo | 3·55 | 3·7 ± 0·08 | 3·71 ± 0·07 |
| CRM-475 | Cr | 14·14 | 14·4 ± 0·30 | 14·3 ± 0·22 |
| | Mn | 0·89 | 0·86 ± 0·02 | 0·96 ± 0·02 |
| | Fe | 75·00 | 75·3 ± 1·70 | 77·0 ± 1·00 |
| | Co | 0·22 | 0·3 ± 0·03 | – |
| | Ni | 5·66 | 5·7 ± 0·15 | 5·63 ± 0·10 |
| | Nb | 0·22 | 0·23 ± 0·02 | – |
| | Mo | 1·59 | 1·61 ± 0·04 | 1·6 ± 0·03 |

**Table 2.** Concentrations of SS-304 and SS-316 samples determined by EDXRF and VES.

| Sample no. | Elements | Concentrations (%) | | |
|---|---|---|---|---|
| | | Certified range | By EDXRF | By VES |
| SS-304 | Cr | 18·0–20·0 | 18·9 ± 0·40 | 18·0 ± 0·27 |
| | Mn | 2·0 Max. | 1·23 ± 0·05 | 1·27 ± 0·03 |
| | Fe | 60·0–70·0 | 69·9 ± 1·60 | 70·0 ± 1·00 |
| | Ni | 8·0–12·0 | 8·9 ± 0·20 | 8·0 ± 0·10 |
| | Cu | – | 0·3 ± 0·01 | – |
| | Nb | – | 131 ± 20·0 ppm | – |
| | Mo | – | 0·6 ± 0·01 | 0·33 ± 0·01 |
| SS-316 | Cr | 16·0–18·0 | 17·5 ± 0·40 | 16·8 ± 0·24 |
| | Mn | 2·0 Max. | 1·56 ± 0·07 | 1·34 ± 0·03 |
| | Fe | 60·0–70·0 | 67·1 ± 1·52 | 67·4 ± 1·00 |
| | Co | – | 0·25 ± 0·02 | – |
| | Ni | 10·0–14·0 | 10·9 ± 0·30 | 10·5 ± 0·20 |
| | Cu | – | 0·28 ± 0·01 | – |
| | Mo | 2·0–3·0 | 2·3 ± 0·05 | 2·23 ± 0·04 |

seen to give good results by the method of analysis reported in this paper.

In general, in XRF analysis of stainless steel types of samples, where several high Z elements are present in sufficiently high concentration, the enhancement effect becomes quite dominant and can give erroneous results if it is not corrected for mathematically. For example in SS, Cr is strongly enhanced by Fe and can yield inflated values for Cr concentration by as much as 40–60% if not properly corrected. In our CATXRF program both matrix absorption and enhancement effects are properly corrected as per the equations given in the theory section.

## 5. Conclusions

In this paper a simple method for non-destructive and standardless analysis of stainless steel samples is presented. The agreement between the calculated concentrations and certified concentration values of various elements in different stainless steel samples have demonstrated that the compositional analysis of stainless steel samples can be made reliably with a simple radioisotope excited EDXRF system. The CATXRF quantitative analysis program in conjunction with the non-linear least square fitting method gives a simple, fast, standardless, nondestructive method of SS analysis. The system described has provided our laboratory with an inexpensive

alternative to the more commonly used VES system for SS analysis. The method reported here can also be used for materials other than steel.

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