ภาคผนวก 1

(ต้นฉบับที่ได้รับการตอบรับลงพิมพ์ใน Journal of Trace and Microprobe Techniques ของ
สำนักพิมพ์ Marcel Dekker และจะปรากฏในฉบับที่ 1 (1999))

Preparation of standards for ilmenite ore by mimicking the ore matrix for EDXRF spectrometry

S. Wongnawa*, P. Boonsin , D. Kongkaew , S. Yodbutra , and S. Pisuttanawat

Inorganic and Mineral Research Laboratory , Department of Chemistry , Faculty of Science , Prince of Songkla University , Hat Yai , Songkla , THAILAND 90112
* for correspondence and reprint requests

Abstract: Composition of ilmenite ore was determined quantitatively by EDXRF spectrometry. Standard materials used to construct the calibration graph when prepared simply by mixing the oxides of the appropriate analyte with binder , usually a starch , would give high base line appearance ,a hump, in the spectrum. The hump base line arises due to high background signal which in turn results from extensive scattering phenomena , especially that of the incoherent (Compton) scattering. In contrast , the ore specimen shows only minor incoherent scattering. In this case the base lines of the standard and the ore specimens are quite different. However , the base line of the standard can be made lower and flat similar to that appears in the ore specimen by adding certain amounts of the major elements (as oxides) into the standards. In this way , the matrices of the standards can be said to be similar to the matrices of the ore specimen.

Keywords : X-ray Fluorescence , X-ray spectrometry , XRF , EDXRF , Ilmenite , titaniferrous ore , sample preparation , geological sample analysis

INTRODUCTION

Base lines in the EDXRF spectra result from the background signals that occur during the spectra acquisition. Sources of this background signal can come from many ways : (i) the elastic and inelastic scattering of Bremsstrahlung (continuous) and characteristic x-rays from the anode by specimens , (ii) the scattering of the two x-rays as in (i) but by various parts of the spectrometer such as the specimen compartment , (iii) the Compton back scattering of x-rays from the Si crystal of the Si(Li) detector [1a , 2a] . Among these the most important is by category (i) , i.e. , scattering by specimens. If the matrix of specimen is composed of low Z elements and is considerably thick the incoherent (Compton) scattering of both Bremsstrahlung and characteristic x-rays can be pronounced and appears as high background at every value of energy [2b] and as scatter peaks.

The large humpy base line would dominate the entire spectrum and overwhelm the analyte spectral lines. If a spectral line locates on the shoulder of the hump reading of the peak intensity will be less accurate to a certain extent as compared to the straight flat base line. Furthermore , in dealing with trace elements the lower limit of detection of trace elements in the specimens are proportional to the square root of background count , e.g. , three times of square root of background [3,9,10] . All these problems lead to the suggestion that the background should be made as low as possible [2b] .

The composition of the specimen matrix has direct effect on the background signal. The matrices that compose mostly of low Z elements , e.g. biological specimens , would have high background signal due to large incoherent scattering of the x-rays whereas the matrices of high Z elements , e.g. some geological and metal specimens , would have little incoherent scattering and thus low background signal [4a] .

Most of the quantitative analyses by EDXRF have been performed by using the calibration graph method. Slight different in the form of data used lead to few variations of this graphical method : (a) the calibration with standard reference materials , (b) the standard addition , (c) the internal standardization ; all of which need a set of standards for the construction of a calibration graph. At any rate , to obtain good results , these methods require large number of standards to help make correction from matrix effect [5,6].

The ability of EDXRF to analyze specimens in solid form presents both strong and weak points at the same time. The strong point is realized when dealing with specimens which are insoluble or nearly insoluble in solvents while the weak point is due to the homogeneity problem for solid specimens. Furthermore , compositions of the matrices of solid powders can be quite diverse ranging from light matrices (of low Z elements) to heavy matrices (of high Z elements). Therefore , a wide range of background signals can be encountered from one solid specimen to another and thus spectra of completely different base lines can be obtained for EDXRF spectrometry. Besides the homogeneities of the specimens , another point of equally important is that the matrices of the standards and the matrices of the unknown specimens must be very similar as much as possible to minimize any additional errors from matrix effect [7,8]. The standard addition method is the method that suits most to this requirement since it gives almost the same type of matrices between the standard and the unknown specimens. This method , however , has some limitation and is not suitable in case of the limited quantity of sample. In addition , eventhough the whole operation of EDXRF spectrometry is usually fully computerized some softwares may not include the capability of handling the standard addition method , for instance , as in our case.

Many suggestions had been given [1b,2c] in an attemp to reduce high background signals , e.g. , (i) to use low excitation conditions (kV , mA) , (ii) to use filters to remove anode lines or to reduce continuum intensity in the region of a specific analyte line , (iii) to reduce the specimen thickness , (iv) to avoid matrix of low Z (as in solutions , fusion products , glass disks) , (v) to avoid using low Z elements as binder , etc. These methods can be applied directly without having to modify the spectrometer. Recently , few other alternatives to reduce background have been accomplished through the modified spectrometer. In one approach the three-axial spectrometer was utilized while the other was based on the polarized x-ray radiation [9,10]. These methods , however , are not applicable to our case. The problems we are facing here is the matrices of standards and those of unknown specimens are quite different as evidence from low background in the unknown specimens but high background in the standards. We , therefore , adopted a method to solve the problem chemically by adjusting the matrix composition of the standard making it resemblance to that of the unknown specimens and thus the same shape of base lines can be obtained.

The elements of concerned in our ilmenite ore are : Ti , Mn , Fe , Y , Zr , Nb , Sn , and W . The quantities of these elements roughly are : Ti , Fe > 10 % ; Mn , Nb , Sn , W between 0.1 - 10 % ; Y , Zr < 0.1 %. Ti and Fe are then classified as major elements ; Mn , Nb , Sn , W as minor elements ; Y and Zr as trace elements [1c,2d] .

In this article the method of preparing standards whose matrix compositions are closely similar to that of unknown specimens will be described. Briefly , ground ilmenite ore was mixed with corn starch (binder) and pressed into pellet disks. This represents the unknown specimen and will be referred to , in this work , as *the ore specimen.* For the standards , they were made up by mixing the oxides of the corresponding metals also with corn starch but a certain amount of the major elements (Ti , Fe in oxide form) were also added and pressed into pellet disks. The addition of major elements into the standards is the key to help adjustment of the standard matrices similar to the matrices of the ore specimens.

MATERIALS AND METHODS

Chemicals

Ilmenite ore is a black lustrous sand of grain size *ca.* -60 mesh. Ore samples had been physically concentrated at the Office of Mineral Resources Region 1 , Songkla , Thailand. The Office in turn received raw ilmenite ores from various mines in the southern part of Thailand , hence , each lot of the sample ore received from this office generally came from different sources. This reflects by their compositions analyzed as shown in Table 2.

All the metal oxides used in the standards preparation were all of analytical grade ; TiO_2 (AR , E.Merck) ; Fe_2O_3 (AG , E.Merck) ; Y_2O_3 , ZrO_2 , Nb_2O_5 , SnO_2 , WO_3 (AG , Fluka) ; MnO_2 (AR , Carlo Erba).These oxides were dried at 110 °C for 3 hrs before used. Corn starch (100 % , CPC/Aji , Thailand) was used as a binder for pressing all the specimens into pellet disks.

Equipment

Orbital shaker (Adgle Kuhner , AG , Switzerland) was used for the mixing of ore specimens or metal oxide standards with corn starch binder. The maximum shaking speed attainable by this unit is 400 cycles per minute (cpm).

Energy dispersive x-ray fluorescence spectrometer (Spectrace 5000 , Spectrace Instruments , Inc. , Mountainview , California) is of the tube type. The tube target is Rh. The detector is the liquid nitrogen cooled Si(Li) with resolution of 164 eV for the Mn Kα line. This spectrometer is fully computerized through the software EDXRF version 1.35 (DOS version) provided by the spectrometer manufacturer. The software has the capability of handling the matrix effect correction. The results are obtained via the conventional calibration graph method. The other optional methods , e.g., the standard addition is not available , however.

Die (SPECAC , Kent , England) of diameter 32 mm together with the hydraulic press (Ring Press 00-25 , Research and Industrial Instruments Co.) were used to press the powder specimens into pellet disks. The pressure used was 8 tons per square inch.

X-ray diffractometer (Philips , PW3710) was used to acquire the XRD spectra and carried out at the Central Equipment Division of the Faculty of Science. The tube target is Cu.

Procedure

(A) Preparation of the ore specimen Ore sample was intimately ground before mixing with corn starch in the ratio 1 : 5 (ore : starch) in 250 ml Erlenmeyer flask. To the flask were added 2-3 pieces of clear plastic blocks , each weighs 1.3 g and of dimension 15 × 9 × 7 mm , to act as the moving stirrers. The content in the flask was shaken on the orbital shaker at 320 cpm[1] for 24 hrs to ensure homogeneity. After shaking the mixed powder was accurately weighed for 4 g and pressed as pellet disk of 32 mm diameter under 8 tons per squre inch pressure.The pellet thus obtained was considered as infinitely thick [1d] . The EDXRF spectra of these ore specimens are shown in Figs 1 and 2 .

(B) Preparation of the standard All the standards were made by using the corresponding metal oxides mixed with binder (corn starch). To each standard were added the "appropriate" amount of TiO_2 and Fe_2O_3 which are the two major elements in the ore specimens. These "appropriate " amounts were obtained by successively varying the amounts of the two majors elements then added to the standards , shaken , and pressed as pellet for spectra acquisitions until the selected Region of Interest (ROI) counts in the resulting standards getting close to those in the ore specimens (from *(A)* above) to within *ca.* ± 10 %.

(C) Spectra acquisition and calculation In acquiring the EDXRF spectrum , the pellet of each specimen was recorded in triplicate , each by 90 ° rotation [11]. Any inhomogeneity , if exists , can be easily detected by this pellet rotation. The tube voltages used were : 15 , 25 , and 40 kV , each value was selected for some certain analytes to ensure the most effective excitation. Most of the peak intensities used were those of Kα lines , except W and Fe. For W the Lα line was used while for Fe the Kβ line was used.
(The Fe Kα was not used due to overlapping with the Mn Kβ line.) [2] Calibration graphs of the standards were constructed through the software EDXRF version 1.35 after which concentrations of analytes in the ore specimens were calculated from these graphs. The software ability to handle the matrix effect correction is worth to be mentioned. After having applied this function a good straight line usually can be obtained. Example of calibration graphs are shown in Figs 7 and 8.

RESULTS AND DISCUSSION

---

[1] The shaking speed can be set differently if stirrered with other materials. For example , when used burundum (Thomas catalog number 3440-G50) the speed can be set at 240-250 cpm. Each burundum weighs 5.5 g and of cylindrical form: 12.5 mm in length × 12.5 mm diameter.

[2] The software does not have the capability to deconvolute the overlap peaks. The use of Fe Kβ peak did not pose any problem since the content of Fe is high and this peak is sufficiently large to minimize the statistical error. On other occasion , not this work , we used to check the result of using Fe Kα and compared with using Fe Kβ on the sample with considerably high Fe content , they gave identical results.

EDXRF spectra of ore specimens , as prepared from Procedure *(A)* , acquired at 25 kV and 40 kV are shown in Figs 1 and 2 , respectively. The considerably low base lines should be noted in these two figures.

In making the standards , if one just simply takes the desired metal oxide(s) and mixes with starch , a high background or base line will show up in the spectrum just as shown in Figs 3 and 4 which correspond to mixtures of SnO_2 (2000 ppm) in starch and WO_3 (800 ppm) in starch , respectively. In Fig 5 the same concentration of SnO_2 (2000 ppm) as that in Fig 3 but with the addition of 4 % TiO_2 , no significant changes yet can be observed. However , in Fig 6 , the same composition of Fig 5 but with the addition of 5.5 % Fe_2O_3 , some drastic changes in the base line can be observed. So we can see that the addition of the two major elements are essential to adjust the matrices of the standards to yield similar low base line to that of the ore specimen. Having gone through series of experiments , the final "appropriate" amounts of TiO_2 and Fe_2O_3 added to each set of standard can be summarized in Table 1.

Each set of the standard composes of 5 concentrations ranging from blank (zero concentration) to the highest value as specified in the second column of Table 1 . Some set of standards contain two elements , instead of only one , to save time during preparations [12] . In such cases , the two elements should be well separated such that their fluorescent peaks would not overlap or interfere with each other. In general , each concentration , among the set of 5 concentrations , contains fixed amounts of TiO_2 and Fe_2O_3 as given in the third and fourth columns of Table 1. However , in the set of Nb_2O_5 and WO_3 standards the amount of TiO_2 and Fe_2O_3 had to be varied , in the range as given in Table 1, to obtain good straight lines for the calibration graph (Fig 7). For Fe_2O_3 standards , the addition of TiO_2 to adjust the matrix composition was very sensitive and difficult to bring the base line to within *ca.* ±10 % of the desired criterion. However , eventhough the base line obtained for Fe_2O_3 standards slightly exceeded the criterion ±10 % , the calibration graph as constructed from these spectra still forms a very good straight line , as shown in Fig 8. Since Fe_2O_3 is present in large amount , it peaks are intense with high counting signal so the error from counting statistics will be small and insignificant.

Tertian and Claisse [4b] give an example of calculation relevant to scattering phenomena and matrices of varying Z's. They cited the spectrometer utilizing Ag Kα (E = 22.1 keV) and scattering angle $\varphi = 90^\circ$ [3] and showed in details the calculation for mass scattering coefficient (σ) for coherent (σ_{coh}) and incoherent (σ_{inc}) scattering from specimen matrices of varying Z's ranging from 3 to 30. The calculated σ_{coh} and σ_{inc} were then plotted against Z's. This graph shows that for low Z σ_{inc} is much larger than σ_{coh} and coalesces as Z approaches 20 after which σ_{coh} becomes larger and diverges as Z keeps increasing. Similar calculation and graph were treated by Kubo and Smythe [13] in an application to measure the mass of biology and medicine samples. (This method was used for samples of very small mass (~ 300 mg) where normal weighing on an analytical balance could cause significant error.) And recently , calculations in this manner were shown , but for higher photon energies , in the atomic number region $12 \leq Z \leq 82$ which gave similar results [14] .

Upon inspection of the ore specimen spectrum in Fig 2 one can see that the intensity of the incoherent peak of Rh Kα is considerably larger than the coherent Rh Kα. This is also true for the same in Figs 3 , 4 , 5 , and 6. Judging from the graph shown by Tertian and Claisse one can conclude that the matrices of all these specimens can be considered as low Z . In the

---

[3] This is a similar configuration to our spectrometer the only different is the tube ; ours is Rh.

ore sample (Figs 1 and 2) , the ore matrix itself will be of high Z but during the specimen preparation 1 g of ore was mixed with 5 g of starch , therefore the effect from the starch will dominate and drastically dilute the ore matrix leading to being a low average Z specimen..

Shown in Table 2 are the concentrations of the main analytes in our three ilmenite samples as determined by using the standards made up as explained above. The three samples are designated as Ilmenite 1 , Ilmenite 2 , and Ilmenite 3 , respectively. As already mentioned , the three samples of ore came from different locations so their compositions are slightly different. Among the three samples , Ilmenite 2 contains the highest percentage of cassiterite (SnO_2) followed by Ilmenite 3 and Ilmenite 1 , respectively. These results are in excellence agreement with the XRD spectra (Fig. 9) where the cassiterite peaks can be seen strongest in Ilmenite 2 and less in Ilmenite 3 while being unobservable in Ilmenite 1.

The compositions of minerals , in general , can vary in a certain range depending on the locations where they were deposited. For ilmenite ($FeTiO_3$) , theoretical TiO_2 content would be 52.66 % . In nature , the content of TiO_2 can vary over a wide range due to presence of other elements or minerals within ilmenite grains and the weathering of iron oxides from the ore. The former would cause lower percentage of TiO_2 content while the latter for higher percentage[15]. Ilmenite deposits from various locations around the world after having been treated , the content of TiO_2 ranges 37 - 63 % [18a]. Judd and Palmer [16] showed data on the composition of ilmenite from many sources , the data can be summarized into ranges of each composition : TiO_2 43.9 - 60.3 % , Fe_2O_3 35.5 - 52.1 % , MnO 0.40 - 1.6 % , etc.[4] The ilmenite from Bangladesh has been cited to contain 27.8 % (wt.) titanium , 32.4 % (wt.) iron and about 12 % (wt.) silicon dioxide[17]. Other reports [18b-21] showed contents of TiO_2 ~ 44 - 55 % , Fe_2O_3 ~ 43 - 50 % , MnO ~ 0.3 - 2 % .[4] No results on the contents of Y_2O_3 , ZrO_2 , Nb_2O_5 , SnO_2 , and WO_3 have been given in these references , however.

The accuracy of the analysis results presented in Table 2 was checked by two different methods. The first was by including one of the working standard along with the ore specimens which were then analysed under the same conditions. The concentrations of analytes found in the standard agreed very well with the known values. For example , for TiO_2 the result came within 1 % of the known value. This is an excellence support for the results reported in Table 2 , especially for the two low values of TiO_2 (Ilmenite 2 and 3). The second method was by the recovery experiments , i.e. , by adding known amount of some selected analytes to the ore specimens and analysing for the new combined concentration values. Four selected analytes added were Y_2O_3 , ZrO_2 , Nb_2O_5 , and WO_3. The specimens were prepared in two series with two different amounts of the added analytes ; roughly about twice of each other. The results again are quite acceptable , the amount added compared very well with the amount found , as shown in Table 3.

It is noteworthy to mention that the working standards as described here give good analysis results only with the ore specimens prepared from 1 g of ore to 5 g of starch (see Procedure *(A)* and *(B)*). We found that by altering the compositions of ore specimens to 0.5 g of ore and 6 g of starch quite different analysis results were obtained , most of them higher than those given in Table 2. (They were analysed simultaneously under the same conditions.) The major elements are 8 - 30 % higher while the minor and trace elements are 20 - 90 % higher with the exception of two items about 60 % lower. The cause of this large error can be explained based on the different matrices in the standard and the new ore specimens. By

---

[4] In these references the contents of Fe were given as two separate species , FeO and Fe_2O_3. The amount of FeO was converted to Fe_2O_3 and shown here as total Fe_2O_3.

comparing their EDXRF spectra , the base lines of the new ore specimens are much higher than those of the standards attesting to their significantly different matrices.

CONCLUSIONS

Sets of standards for quantitative analyses by EDXRF spectrometry were prepared by using oxides of the corresponding analytes mixed with starch plus certain amount of the major elements. The matrices of these standards as prepared simply mimic those (matrices) of the unknown specimens. The similarity of the standard and the unknown matrices are of prime important in x-ray spectrometry and this can be quickly distinguished through their base lines appearance.

Acknowledgements

This work is supported by the research grant from the Faculty of Science , Prince of Songkla University. We are indebted to Dr.Kamnoon Kanchanapoom of the Department of Biology for use of the orbital shaker. Most important of all we would like to express our appreciation to the International Atomic Energy Agency (IAEA) for their support in providing the EDXRF spectrometer (Project Code : THA/2/008).

REFERENCES

1. Bertin EP (1978) *Introduction to X-ray spectrometric analysis* , Plenum Press , New York ; (a) p.224 (b) p.226 (c) p.84 (d) pp.351-352.
2. Jenkins R , Gould RW , and Gedcke D (1981) *Quantitative X-ray spectrometry* , Mercel Dekker , Inc., New York ; (a) p.502 (b) p.525 (c) p.53 (d) p.500.
3. Yap CT (1993) Radioisotope-excitation XRF determination of trace elements in marble , *Appl.Spect.* , **47**, 330-333.
4. Tertian R and Claisse F (1982) *Principles of quantitative X-ray fluorescence analysis* , Heyden & Son Ltd. , London ; (a) p.23 (b) p.31.
5. Giauque RD, Garrett RB , and Goda LY (1979) Determination of trace elements in light element matrices by X-ray fluorescence spectrometry with incoherent scattered radiation as an internal standard , *Anal. Chem.* , **51** , 511-516.
6. Matsumoto K and Fuwa K (1979) Major and trace elements determination in geological and biological samples by energy dispersive X-ray fluorescence spectrometry , *Anal. Chem.* , **51** , 2355-2358.
7. Nielson KK (1977) Matrix corrections for energy dispersive X-ray fluorescence analysis of environmental samples with coherent /incoherent scattered X-rays , *Anal. Chem.*, **49** , 641-648.
8. Tindall GW (1977) Effect of matrix composition on line intensity in the determination of light elements in organic compounds by X-ray fluorescence spectrometry , *Anal. Chem.* , **49** , 1403-1405.
9. Viksna A and Selin E (1996) Intercomparison between energy dispersive and total reflection X-ray fluorescence in whole blood analysis , *J.Trace Microprobe Techn.* , **14** , 763-774.
10. Heckel J (1995) Using Barkla polarized X-ray radiation in energy dispersive X-ray fluorescence analysis (EDXRF) , *J.Trace Microprobe Techn.*, **13** , 97-108.

11. Yap CT (1988) X-ray total reflection fluorescence analysis of iron , copper , zinc , and bromine in human serum , *Appl.Spect.*, **42** , 1250-1253.
12. Yap CT and Hua Y (1994) Experimental studies in EDXRF on a new linear relationship for fluorescence , *Appl. Spect.*, **48** , 1394-1398.
13. Kubo H and Smythe WR (1979) X-ray measurement of X-ray fluorescence sample mass , *Anal.Chem.*, **51** , 1194-1196.
14. Rao DV, Cesareo R , and Gigante GE (1996) Elastic and Compton scattering cross sections in the atomic region $12 \leq Z \leq 82$, *Appl.Radiat.Isot.* , **47** , 219-227.
15. Henn JJ and Barclay JA (1970) Information circular 8450 , Bureau of Mines , U.S. Department of the Interior.
16. Judd B and Palmer EC (1973) Production of titanium dioxide from ilmenite of the West Coast , South Island , New Zealand , *Proc. Australas.Inst.Min.Metall.*, **247**, 23-33.
17. Biswas RK, Habib MA , and Dafader NC (1992) A study on the recovery of titanium from hydrofluoric acid leach solution of ilmenite sand , *Hydrometallurgy* , **28** , 119-126.
18. Darby RS and Leighton J (1977) *Titanium Dioxide Pigments* in *The Modern Inorganic Chemicals Industry* , edited by R. Thompson , The Royal Society of Chemistry , London ; (a) p. 358 (b) p.360.
19. Girgin I and Turker L (1986) Hydrochloric acid leaching of ilmenite - effect of alcohol species , *Bull.Proc.Australas.Inst.Min.Metall.* , **291** , 61-64.
20. Girgin I. (1990) Leaching of ilmenite in HCl -H_2O , HCl- CH_3OH - H_2O and HCl - CH_3OH solutions , *Hydrometallurgy* , **24** , 127-134.
21. Pong,T.K., Besida J , O'Donnell TA , and Wood DG (1995) A novel fluoride process for producing TiO_2 from titaniferrous ore , *Ind.Eng.Chem.Res.*, **34** , 308-313.

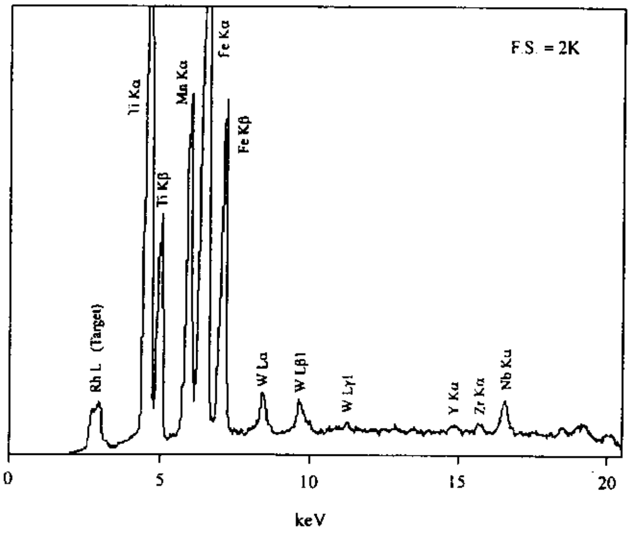

FIG. 1 EDXRF spectrum of ilmenite ore. (Operating conditions : 25 kV, 0.01 mA , 50 s , no filter.)

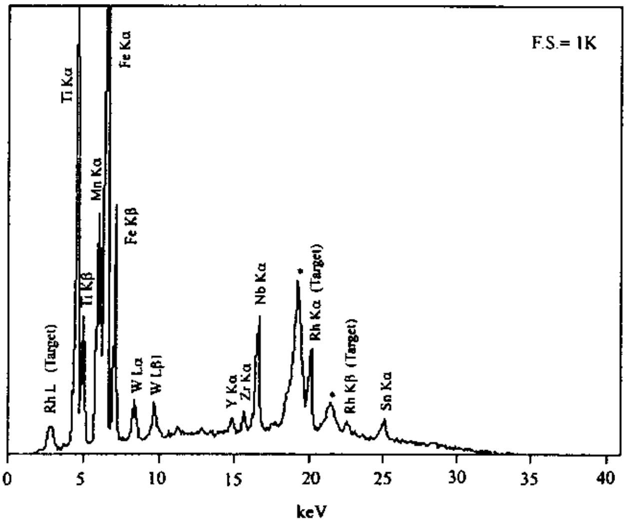

FIG. 2 EDXRF spectrum of ilmenite ore. (Peaks marked with * are the incoherent scattered peaks of Rh K lines.) (Operating conditions : 40 kV , 0.01 mA , 10 s , no filter.)

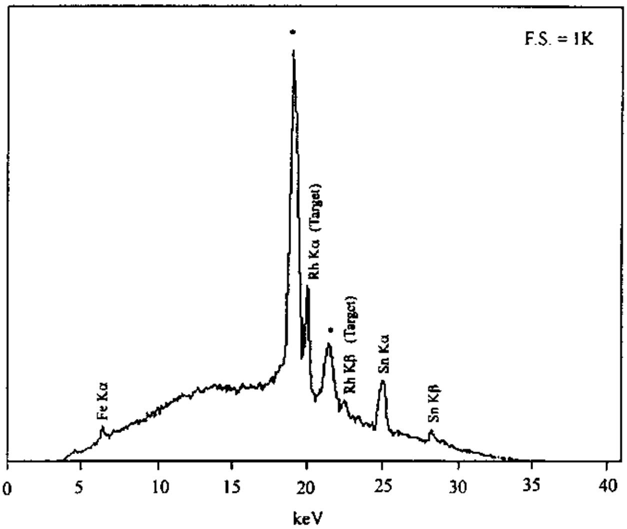

FIG. 3 EDXRF spectrum of mixed powder prepared from SnO_2 (2000 ppm) and starch. (Fe Kα line results from trace Fe in the starch , peaks marked with * are the incoherent scattered peaks of Rh K lines .) (Operating conditions : 40 kV, 0.01 mA , 10 s , no filter.)

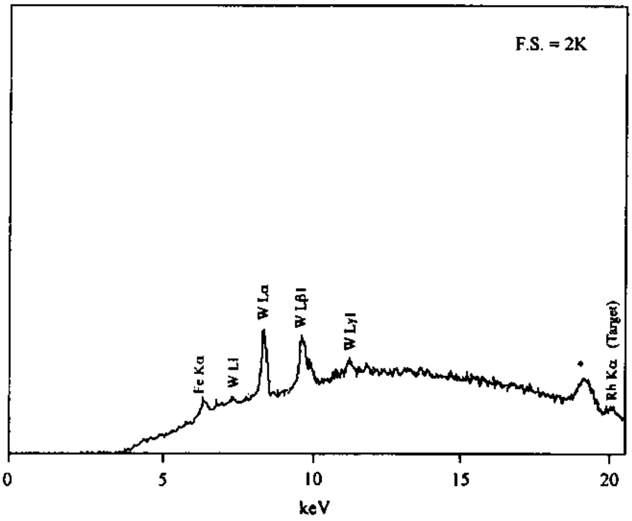

FIG. 4 EDXRF spectrum of mixed powder prepared from WO_3 (800 ppm) and starch. (Fe Kα line results from trace Fe in the starch , peak marked with * is the incoherent scattered peak of Rh Kα line.) (Operating conditions : 25 kV, 0.01 mA , 50 s , no filter.)

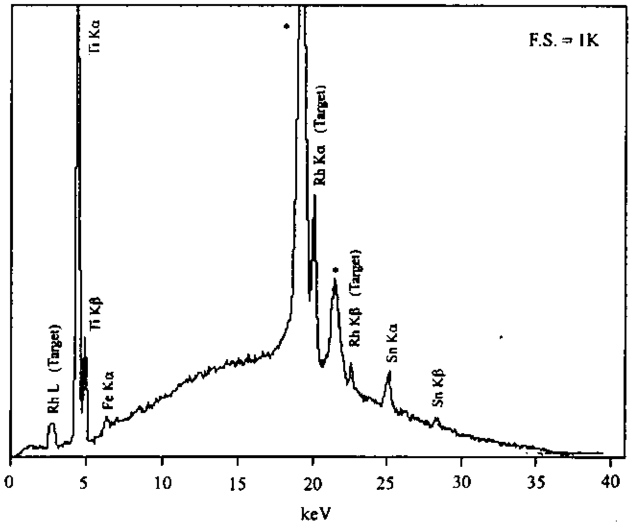

FIG.5 EDXRF spectrum of mixed powder prepared from SnO_2 (2000 ppm) + TiO_2 (4 %) and starch. (Fe Kα line results from trace Fe in the starch , peaks marked with * are the incoherent scattered peaks of Rh K lines.) (Operating conditions : 40 kV, 0.01 mA , 10 s , no filter.)

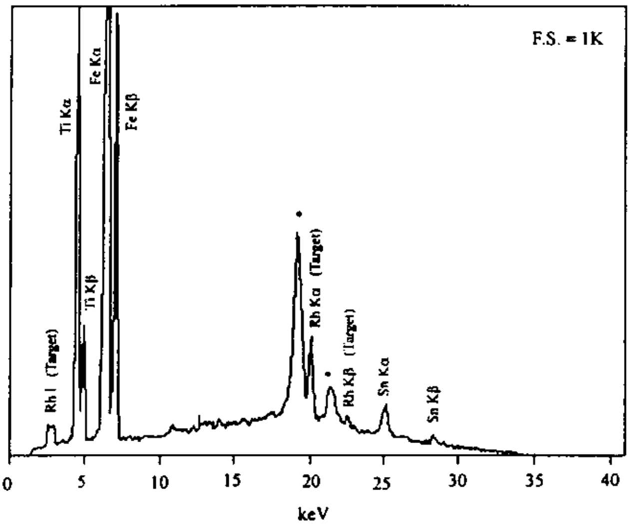

FIG. 6 EDXRF spectrum of mixed powder prepared from SnO_2 (2000 ppm) + TiO_2 (4 %) + Fe_2O_3 (5.5 %) and starch. (Peaks marked with * are the incoherent scattered peaks of Rh K lines.) (Operating conditions : 40 kV, 0.01 mA , 10 s , no filter.)

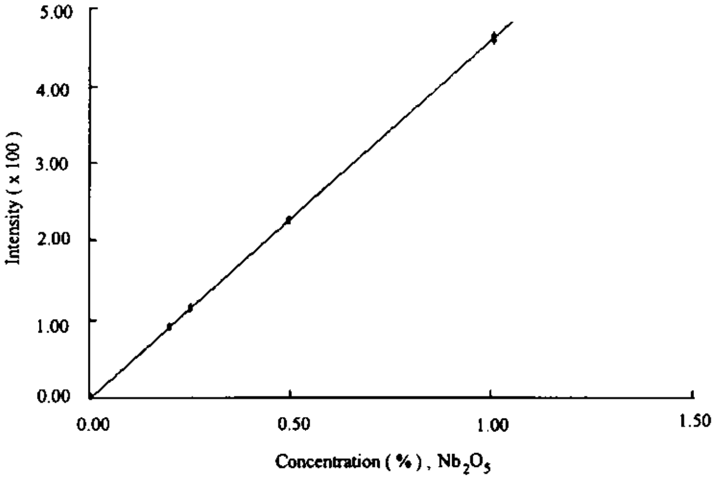

FIG. 7 Calibration graph of Nb_2O_5 standards (as prepared in Table 1).

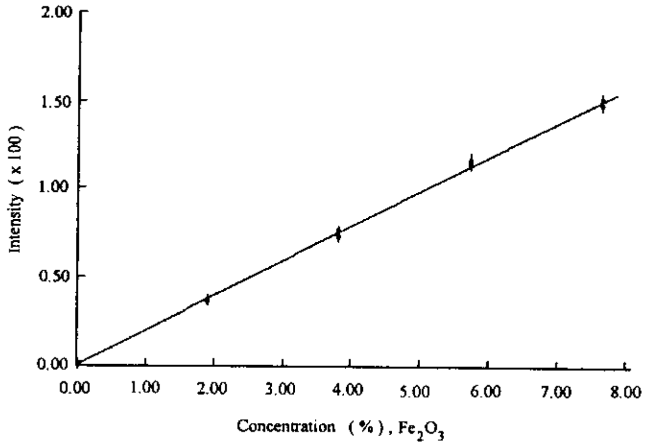

FIG. 8 Calibration graph of Fe_2O_3 standards (as prepared in Table 1).

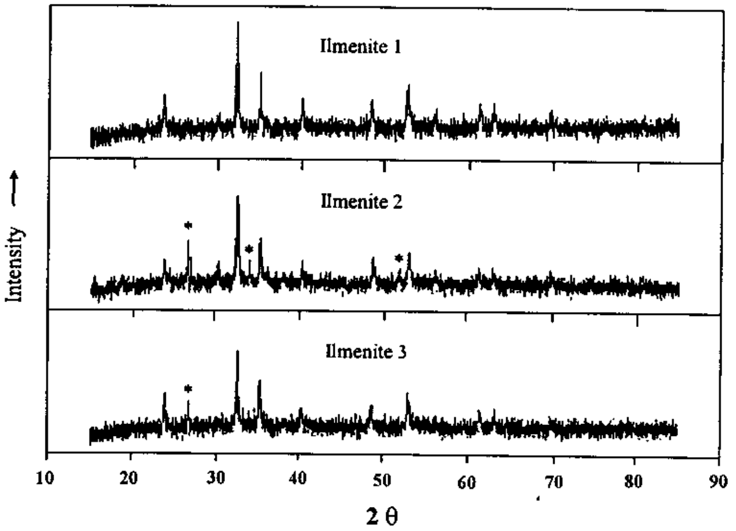

FIG. 9 XRD spectra of three samples of ilmenite ore from different locations. (Peaks marked with * are those of cassiterite , SnO_2.)

TABLE 1

The "appropriate" amounts of major elements (TiO_2 and Fe_2O_3) added to each set of standards.

Analyte (oxide form)	Conc. Range of Standard	TiO_2 Added (%)	Fe_2O_3 Added (%)
TiO_2	0 - 8 %	-	7.5
MnO_2	0 - 2000 ppm	4.5	5.6
Fe_2O_3	0 - 8 %	7.5	-
Y_2O_3	0 - 1200 ppm	6	7
ZrO_2	0 - 2000 ppm	6	7
Nb_2O_5	0 - 1 %	3.5 - 6	4.5 - 7
SnO_2	0 - 2000 ppm	6.5	7.5
WO_3	0 - 2 %	3.5 - 6	4.5 - 7

TABLE 2

Compositions of ilmenite ores from three different locations.

Ore specimen	TiO_2 %	Fe_2O_3 %	MnO %	Y_2O_3 ppm	ZrO_2 ppm	Nb_2O_5 %	SnO_2 %	WO_3 %
Ilmenite 1	46.01	37.05	5.41	688	1117	0.42	0.85	1.73
Ilmenite 2	34.07	48.72	3.67	456	957	0.33	4.44	3.82
Ilmenite 3	35.24	44.65	4.08	419	529	0.21	1.91	1.07

TABLE 3

Recovery of four added analytes.

Ore specimen	Series	Y_2O_3 (ppm)		ZrO_2 (ppm)		Nb_2O_5 (ppm)		WO_3 (ppm)	
		Added	Found	Added	Found	Added	Found	Added	Found
Ilmenite 1	1	78	81	79	106	166	156	156	171
	2	148	157	146	146	294	301	295	286
Ilmenite 2	1	79	68	80	80	156	185	167	144
	2	148	134	148	128	298	271	300	309
Ilmenite 3	1	79	72	80	79	158	150	158	145
	2	149	166	149	153	294	290	299	292