3 RESULTS

3.1 Leaching methods to upgrade ilmenite ore

3.1.1 Main procedure (method A)

The leaching of ilmenite ore by method A was investigated by studying the effect of temperature and initial ilmenite ore to acid ratio.

3.1.1.1 Effect of temperature

The effect of temperature on the leaching of ilmenite ore by method A was investigated by varying temperature at round bottom flask and soxhlet, using 15 g of ilmenite ore and 600 mL of concentrated hydrochloric acid. The result after leaching was summarized in Table 3.

3.1.1.2 Effect of ratio of ilmenite ore to acid

The effect of initial ilmenite ore to acid ratio on the leaching by method A was investigated in 600 mL of concentrated hydrochloric acid by varying the weight of ilmenite ore. The temperature of round bottom flask and soxhlet were kept constant at 105 and 120 $^{\circ}$C, respectively. The results after leaching were summarized in Table 4.

Table 3 Residues after leaching by method A by varying temperature at round bottom flask and soxhlet

No.	Temperature at round bottom flask (°C)	Temperature at outer side of soxhlet (°C)	Leaching time (hrs)	Weight of residue (g)	Residue appearance	Level of blackness*
1	93	80	100	6.4326	small grayish black granule	+++++
2	97	80	57	6.3180	small grayish black granule	+++++
3	97	120	65	6.1754	small yellow granule mixed with brownish granule	++++
4	105	120	65	4.8399	small yellow granule mixed with brownish granule	+++

* the sample of residue color at each level of blackness was shown in Figure 10.

Table 4 Residues after leaching by method A by varying the ratio of ilmenite ore to acid

code	Weight of ilmenite ore (g)	Volume of acid (mL)	Leaching time (hrs)	Weight of residue (g)	Residue appearance	Level of blackness
Am5	5.0214	600	46	1.0663	small yellow granule mixed with brownish black granule	++
Am10	10.0016	600	48	4.7013	small yellow granule mixed with brownish black granule	+++
Am15	15.0488	600	65	4.8314	small yellow granule mixed with brownish black granule	+++

* the sample of residue color at each level of blackness was shown in Figure 10.

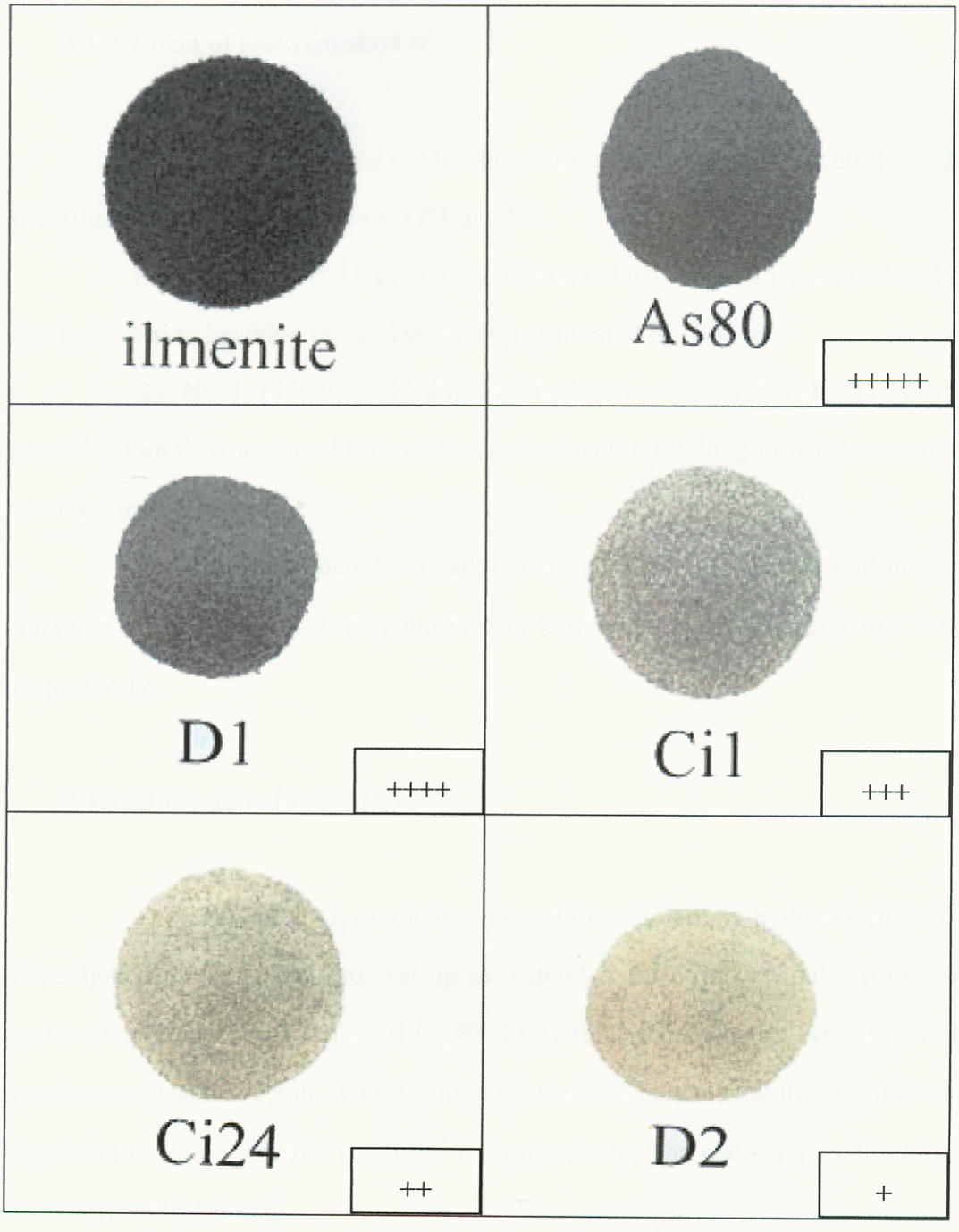

Figure 10 Residue colors at each level of blackness.

3.1.2 Effect of NaCl (method B)

The effect of NaCl on the leaching of ilmenite ore by hydrochloric acid was investigated in two different routes B1 and B2.

B1, ilmenite ore, 15 g, was mixed with NaCl, 5 and 15 g, in sintered glass and subjected to leaching by the same set up as method A.

B2, NaCl, 15 g, was added into 600 mL of concentrated hydrochloric acid in round bottom flask and used this mixture as leachant to leaching ilmenite ore using the same set up as method A.

Table 5 shows detailed conditions of each of the leaching and the results obtained. The temperatures of round bottom flask and soxhlet were 105 and 120 ^{o}C, respectively.

3.1.3 H_2O_2 effect (method C)

The effect of H_2O_2 on the leaching of ilmenite ore by hydrochloric acid was investigated by using the same set up as method A for 65 hours. After filtration the residue was infused in 30 ml of H_2O_2 40 % w/v for 1 and 24 hours. After infusion the residue was leached again by using the same set up. The temperature of round bottom flask and soxhlet were 105 and 120 ^{o}C, respectively. The residue after leaching was summarized in Table 6.

Table 5 Detailed conditions of the leaching to study the effect of NaCl (method B)

Method	Code	wt.NaCl (g)	Leaching time (hrs)	Weight of residue (g)	Residue appearance	Level of blackness*
B1	B1Na5	5.0188	48	6.6659	small yellow granule mixed with brownish black granule	+++
	B1Na15	15.0302	42	7.0298	small yellow granule mixed with brownish black granule	+++
B2	B2	15.1777	50	2.8855	small yellow granule mixed with brownish black granule	++

* the sample of residue color at each level of black was shown in Figure 10.

Table 6 Detailed conditions of the leaching to study the effect of H_2O_2 (method C).

code	Leaching time before infusion(hrs)	Infusion time(hrs)	Leaching time after infusion(hrs)	Weight of residue (g)	Residue appearance	Level of blackness*
Ci1	65	1	53	4.8263	small yellow granule mixed with brownish black granule	+++
Ci24	65	24	48	4.0547	small yellow granule mixed with brownish black granule	++

* the sample of residue color at each level of black was shown in Figure 10.

Table 7 Residues after leaching by methods D1, D2, E, AA, CA and F

method	Leaching time (hrs)	Weight of residue (g)	Residue appearance	Level of blackness*
D1	48+48	3.8811	small yellow granule mixed with brownish granule	++++
D2	48+48	5.3544	small yellow granule mixed with brownish granule	+
E	120	8.1915	small black granule	+++++
AA	65+24	3.7193	small yellow granule mixed with brownish granule	+
CA	65+24+24	4.8783	small yellow granule mixed with brownish granule	+
F	24	3.2775	small yellow granule mixed with brownish granule	+

* the sample of residue color at each level of black was shown in Figure 10.

3.1.4 Other methods

In each method, ilmenite ore, 15 g, was leached by 600 mL of concentrated hydrochloric acid and set temperature at round bottom flask and soxhlet at 105 and 120^{o}C, respectively. The residues after leaching were shown in Table 7. All methods had some white precipitate formed in round bottom flask. In method D1 the amount of white precipitate formed the most. The amount of white precipitate, however, was almost negligible when compared with the residue remained in the sintered glass.

3.1.5 Method F

In this method the effect of temperature of leachant, temperature at outer side of soxhlet, initial ilmenite ore to acid ratio, and leaching time were studied. The elements Fe and Mn remained in the residues after leaching were determined.

3.1.5.1 Temperature of leachant

The effect of temperature of leachant for the leaching ilmenite ore by method F was investigated by varying temperature of the leachant. The initial ratio of ilmenite ore to acid were 15 g ilmenite ore to 600 mL concentrated hydrochloric acid, temperature at the outer side of soxhlet was 120^{o}C and leached for 24 hours. After leaching, the amount of Fe and Mn (Table 8) remained in the residues were determined.

Table 8 Data resulting from effect of leachant temperature.

Temperature of leachant (^{o}C)	% Fe	% Mn
98	8.42	1.55
112	1.42	1.10

3.1.5.2 Temperature at the outer side of soxhlet

The effect of temperature at the outer side of soxhlet of the leaching ilmenite ore by method F was investigated by varying temperature at the outer side of soxhlet. After leaching the amount of Fe and Mn remained in the residues were determined. The data are shown in Table 9.

Table 9 Data resulting from effect of the outer side of soxhlet temperature.

temperature(^{o}C)*	% Fe	% Mn
80	12.12	2.55
90	6.80	2.38
100	2.20	1.12
110	1.95	1.13
120	1.52	1.85
130	1.50	1.54

*Temperature was read from the thermocouple panel.

3.1.5.3 Initial ilmenite ore to acid ratio

The effect of initial ilmenite ore to acid ratio for the leaching of ilmenite ore by method F was investigated by varying weight of ilmenite used. After leaching, the amount of Fe and Mn remained in residues, shown in Table 10, were determined.

Table 10 Data resulting from effect of initial ilmenite ore to acid ratio.

Ore weight (g)	% Fe	% Mn
10	1.52	1.85
15	1.50	1.10
20	2.27	1.22

3.1.5.4 Leaching time

The effect of leaching time for the leaching ilmenite ore by method F was investigated by varying leaching time. The amount of Fe and Mn remained in residues after leaching were determined. The data are shown in Table 11.

Table 11 Data of resulting from effect of leaching time

Leaching time (hrs.)	% Fe	% Mn
12	5.63	2.09
17	3.60	1.61
24	1.52	1.94
30	1.57	1.85

3.2 Measurement of temperature at the soxhlet

This experiment was to measure the temperature at the soxhlet. It was investigated in two different methods. 1) No cover on the soxhlet and 2) cover the soxhlet with beaker as shown in Fgure 9. The results of temperature measurement are shown in Table 12.

Table 12 The temperature measurement in soxhlet in A) no cover on the soxhlet B) cover the soxhlet with beaker. (Temperature of water in round bottom flask was 104°C.)

Temperature set (°C)	Temperature measurement (°C)	
	A	B
100	78	100
110	84	100
120	87	100
130	90	-

3.3 Determinations of acid concentrations

The determinations of acid concentrations (fresh concentrated hydrochloric acid, blank experiment and leachant liquor) were carried out. The blank experiment was set up as in method A and method F without the mineral. In this experiment the system was refluxed for 2 hours and sample of acid was drawn for the titration and the rest was allowed to reflux for 65 hours for method A or 24 hours for method F and the acid was aliquoted for another titration. The leachant aliquots were from the experiment which was set up as in method A with ilmenite added. Aliquots of acid were drawn for titration at 2 hours and 65 hours as in the previous experiment. The method to determine acid concentration was as follows. Diluted sample solution to a proper concentration, then titrated with standard solution NaOH and the pH was measured at every 1 mL of NaOH added. The end point was obtained from this titration plot. The sample of titration curve was shown in Figure 11 and summary data from the determination of acid concentration was shown in Table 13.

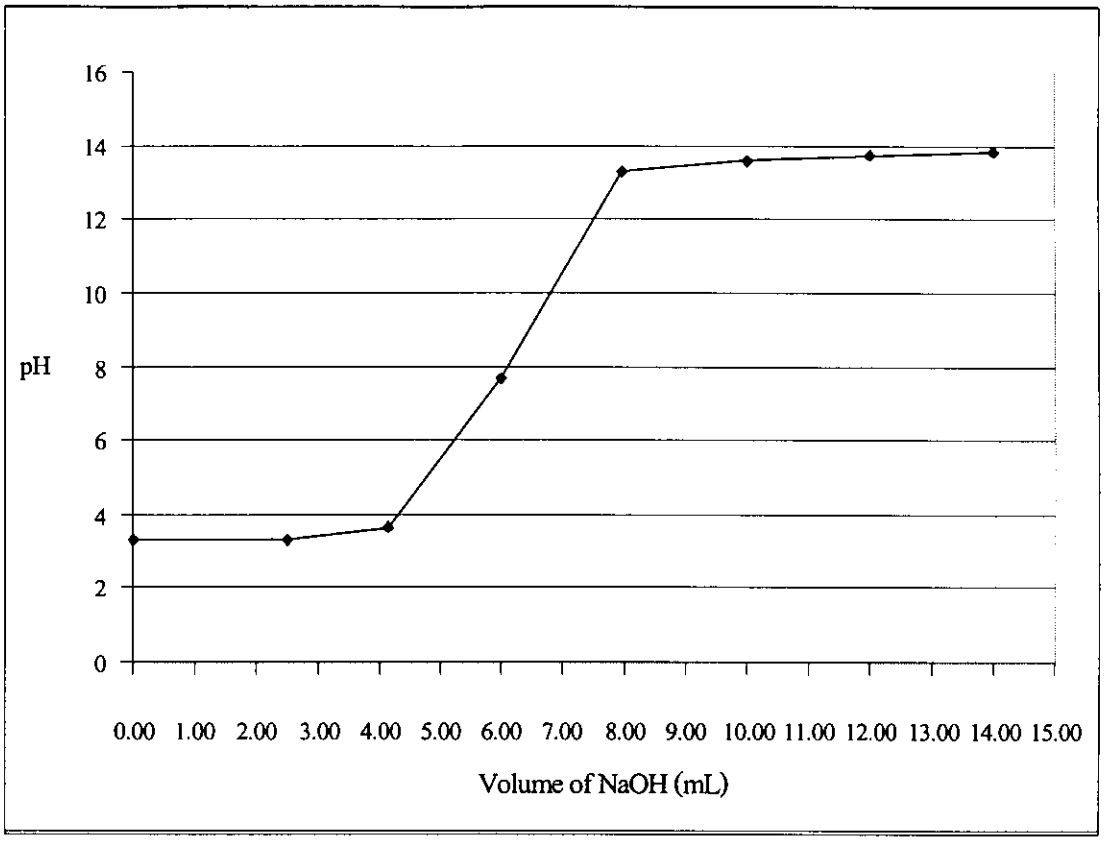

Figure 11 Titration curve of acid determination in soxhlet on blank experiment in method A after reflux 2 hours.

Table 13 Acid concentration.

Method	Sample	Reflux time (hrs.)	$[H^+]$ (mol/L)	
			Soxhlet	Round bottom flask
A	Blank	2	6.86	6.90
		65	3.76	5.94
	Leach liquor	2	6.92	6.97
		65	2.43	6.10
F	Blank	2	10.08	9.96
		24	9.80	6.19
	Leach liquor	2	9.99	10.04
		24	6.19	5.92
Fresh acid (from bottle)			12.31	

3.4 Qualitative analysis by energy dispersive x-ray fluorescence (EDXRF)

X-ray fluorescence (XRF) is one of the most widely used of all analytical methods for the qualitative identification of element having atomic numbers greater than oxygen (>8); in addition, it is often employed for semi-quantitative or quantitative element analyses as well (Skoog and Leary, 1992).

In this work, the element compositions of the starting ilmenite ore and the residues after leaching were analyzed using acquisition parameters as follows.

Tube voltage	:	20	keV
Tube current	:	0.01	mA
Live time	:	30	sec
Max energy	:	20	keV
Filter used	:	No filter	
Preset count	:	0	K
Atmosphere	:	Air	

The EDXRF spectra of starting ilmenite ore, the residue after leaching and white precipitate formed in round bottom flask are shown in Figures 12-18.

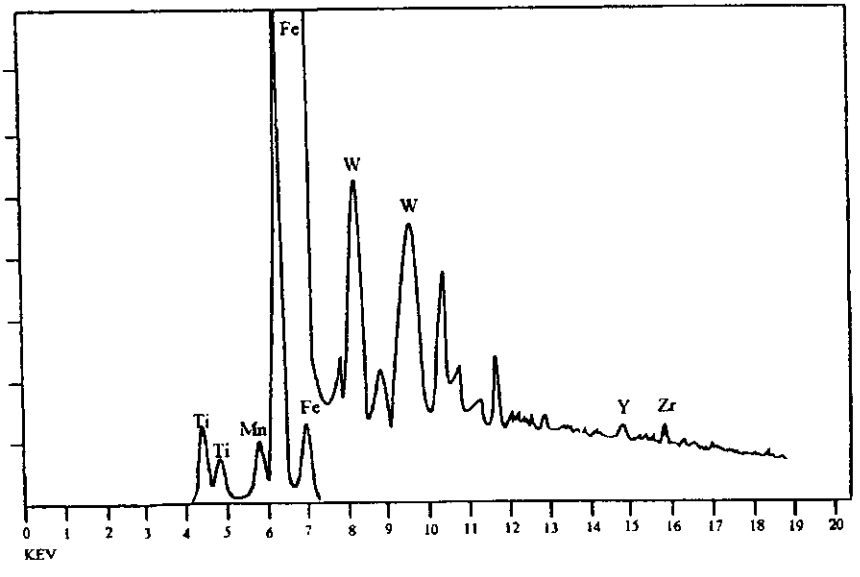

Figure 12 EDXRF spectrum of an ilmenite ore before leaching. Upper trace is enlarged 64-fold.

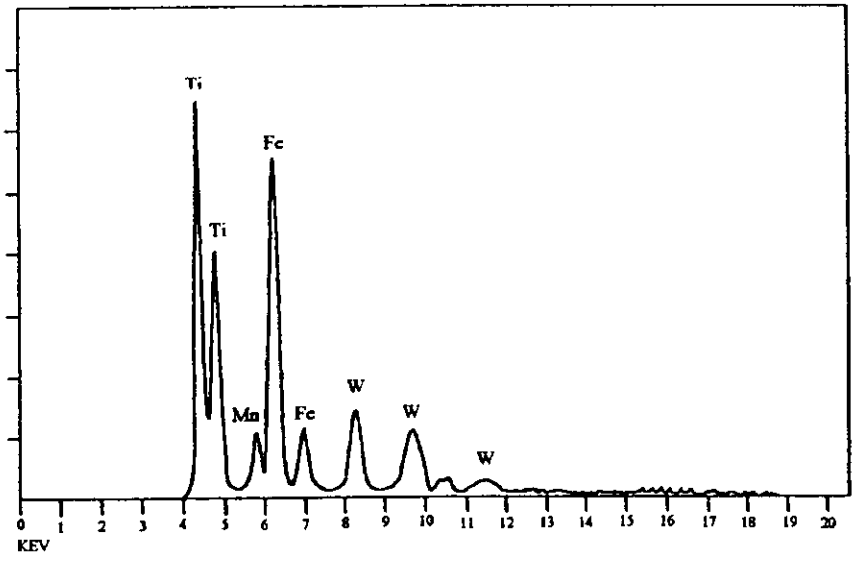

Figure 13 EDXRF spectrum of the residue after leaching by Method A using ilmenite 15 g temperature at round bottom flask and soxhlet were 105 and 120°C, respectively.

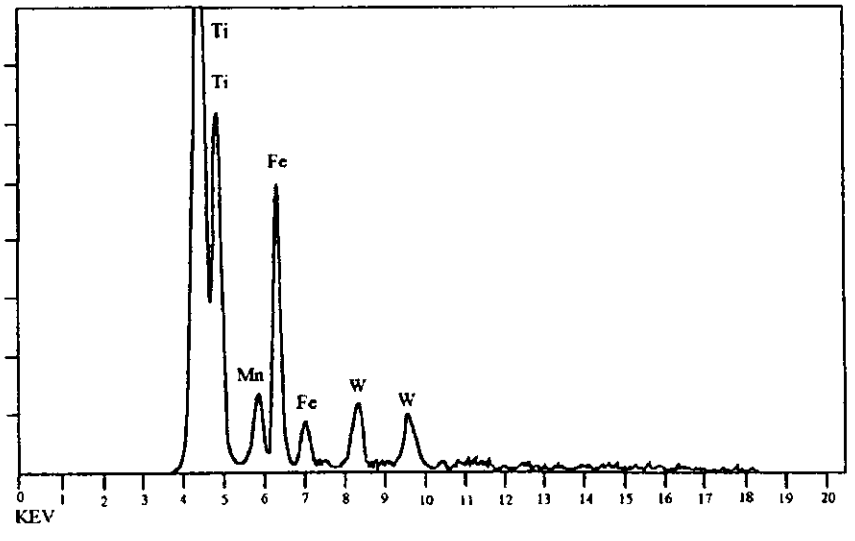

Figure 14 EDXRF spectrum of the residue after leaching by method B1.

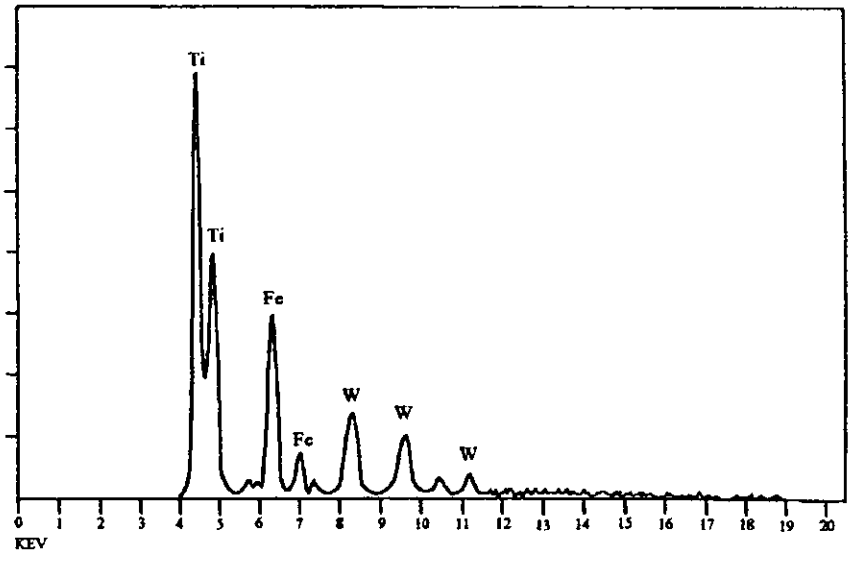

Figure 15 EDXRF spectrum of the residue after leaching by method Ci1.

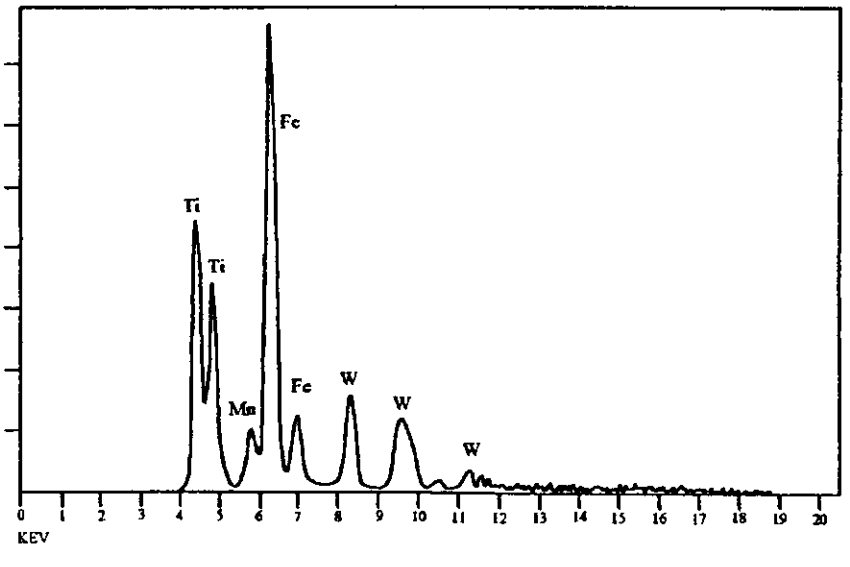

Figure 16 EDXRF spectrum of the residue after leaching by method D1.

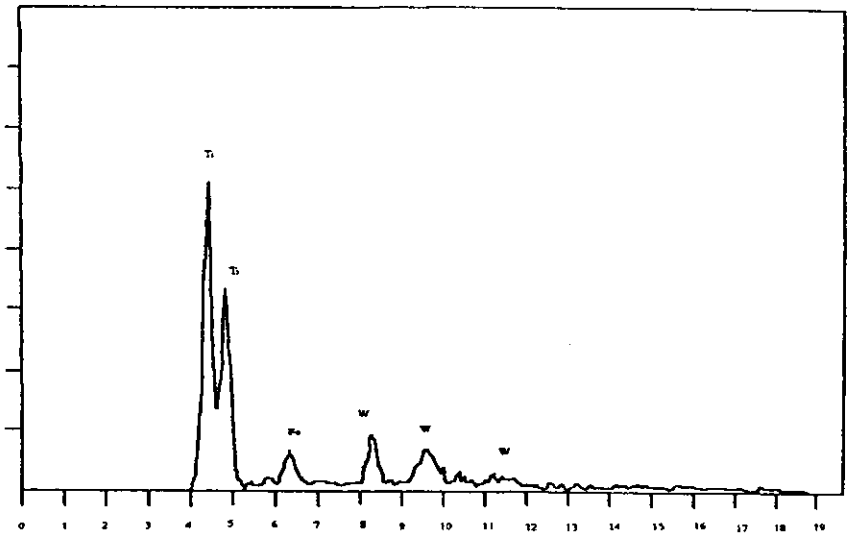

Figure 17 EDXRF spectrum of the white precipitate occurred in round bottom flask after leaching ilmenite ore by method D1.

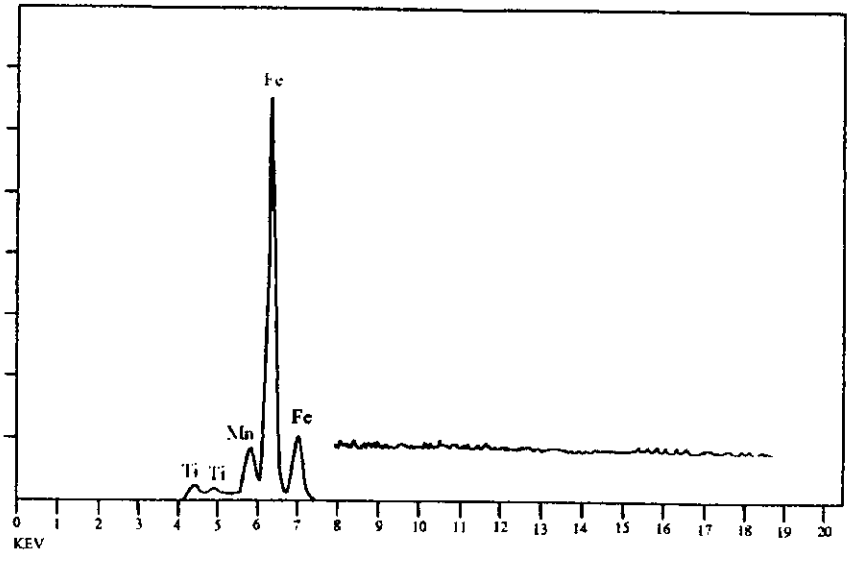

Figure 18 EDXRF spectrum of precipitated obtained from adding 0.1 M NaOH to leachant. Upper trace is enlarged 32-fold.

3.5 X-ray powder diffraction pattern (XRD)

X-ray Powder Diffraction is a method in which a beam of x-rays is directed at a fine powder of randomly oriented grains of crystalline substances. The x-rays are scattered in directions that depend on the crystal structure of the sample and the resulting x-ray diffraction pattern is unique for each crystalline material.

In this work, x-ray diffraction analysis was used to determine the phases present in both starting ilmenite ore, some of the final residue of the leaching test and the white precipitate formed in round bottom flask after leaching ilmenite ore by method D1. They are shown in Figures 19-23.

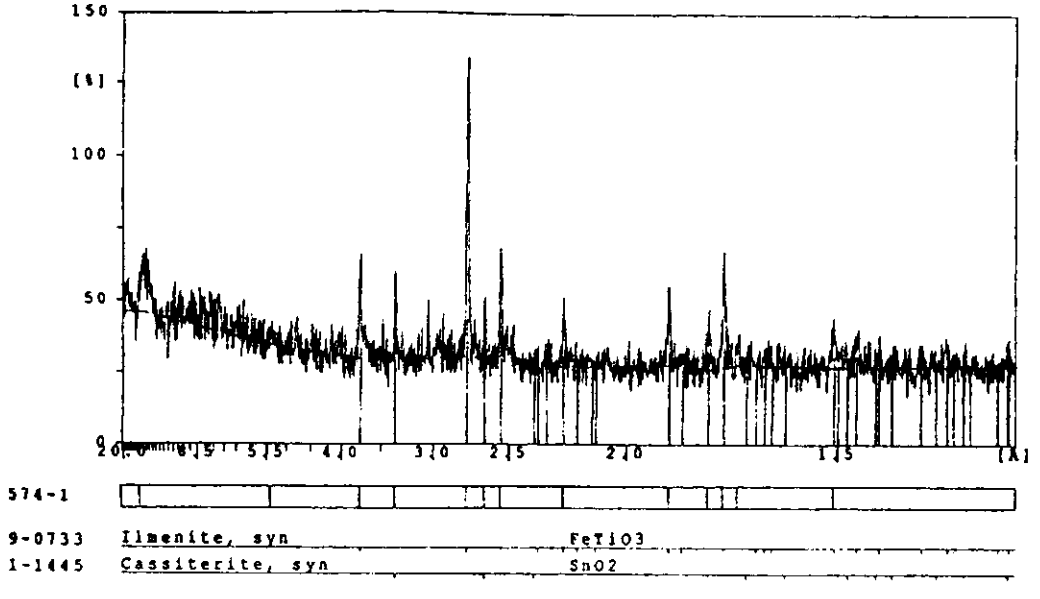

Figure 19 XRD spectrum of starting ilmenite ore.

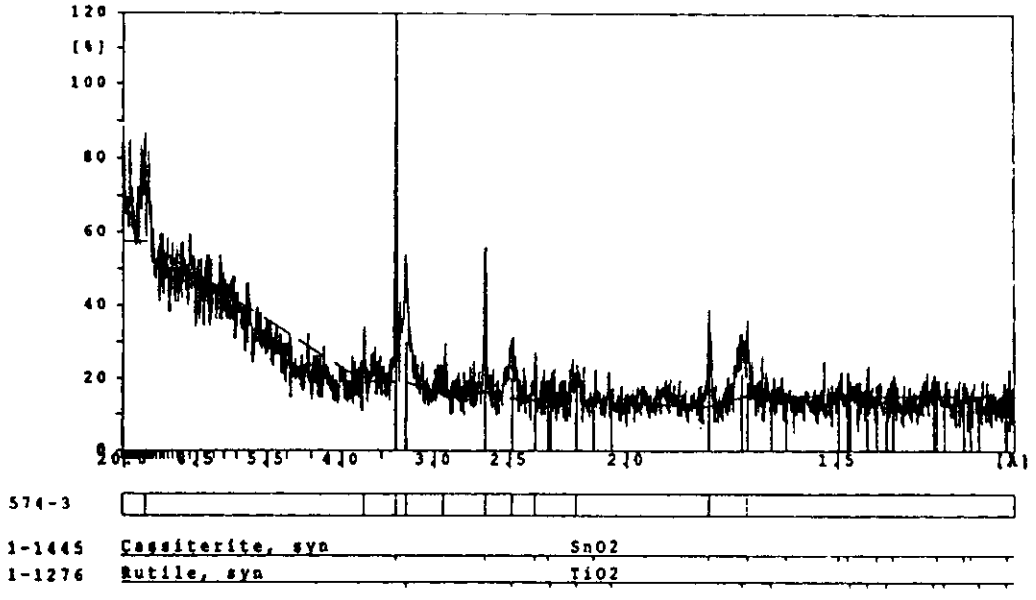

Figure 20 XRD spectrum of the residue after leaching by method AA.

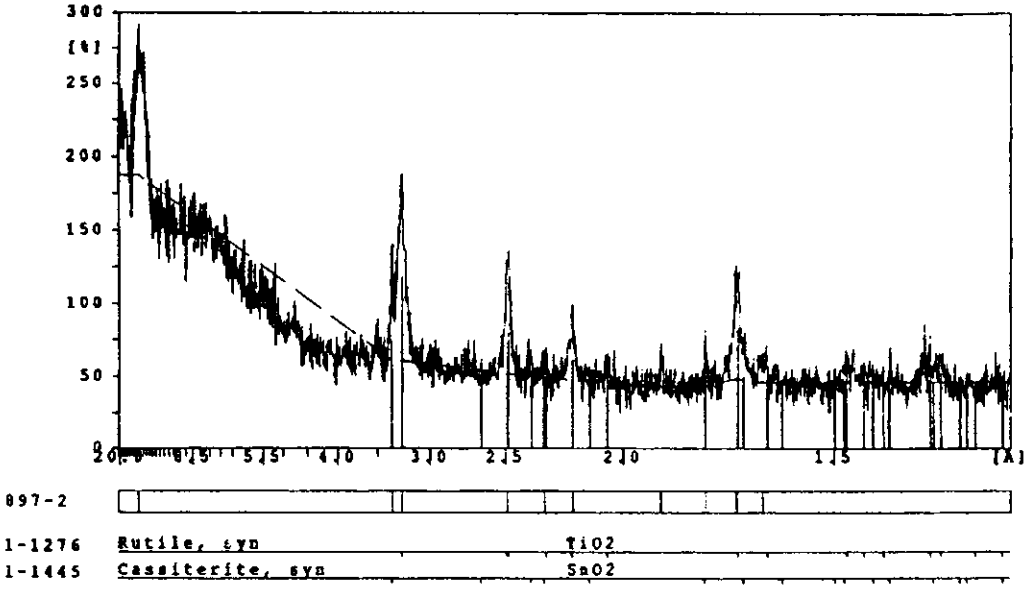

Figure 21 XRD spectrum of the residue after leaching by method CA.

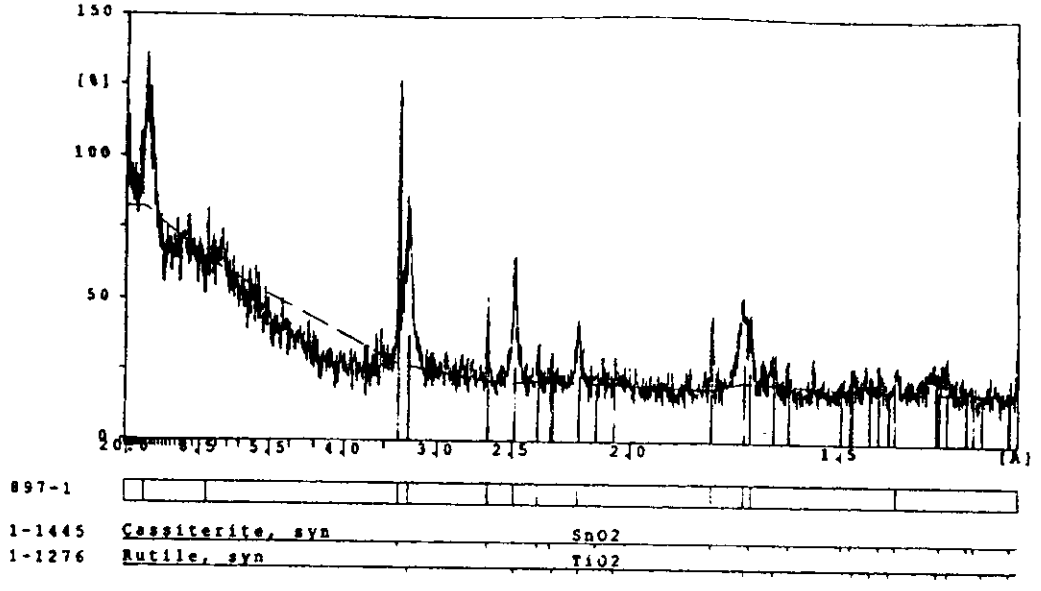

Figure 22 XRD spectrum of the residue after leaching by method B1.

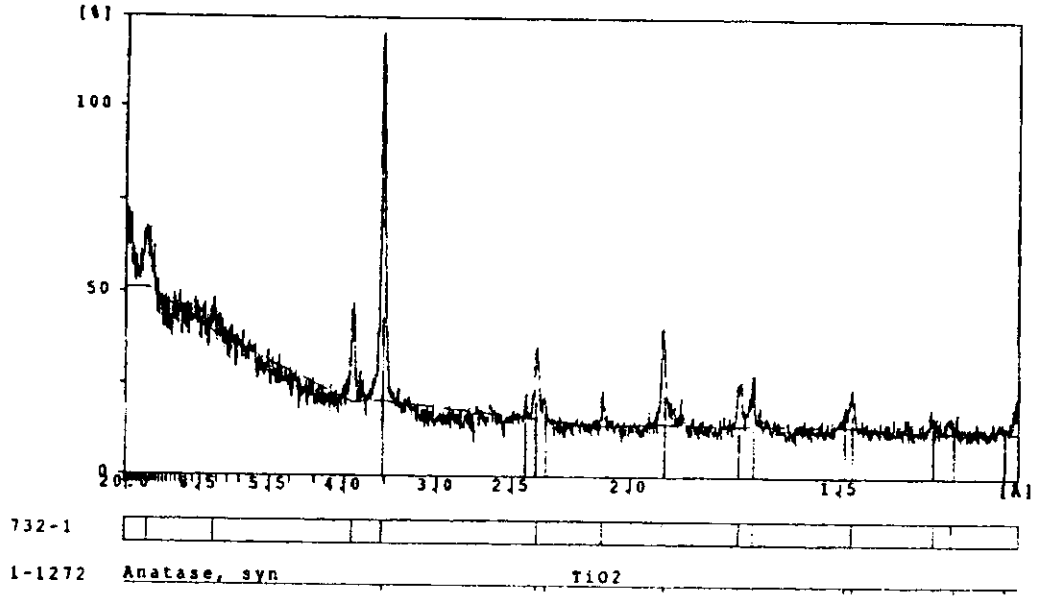

Figure 23 XRD spectrum of the white precipitate occurred in round bottom flask after leaching ilmenite ore by method D1.

3.6 Quantitative analysis by wavelength dispersive x-ray fluorescence (WDXRF)

X-ray fluorescence is an excellent method for the qualitative and quantitative determination of the major and important trace elements in geological materials. It is recognized as a precise and reproducible method.

For x-ray fluorescence analysis the sample material is irradiated with x-rays, which excited secondary x-ray fluorescence. The secondary x-ray has characteristic wavelengths produced by the elements of the sample material. The separation of individual wavelengths of the fluorescent x-ray emission is done by Bragg diffraction from crystals of particular lattice spacing. Through measurement of these characteristic wavelengths, the qualitative composition of the sample can be determined. The intensity of the fluorescent radiation allows the determination of the element concentrations in the sample.

The linear calibration curves for each element (Fe, W, Y, Mn, Sn, Zr, Nb) are shown in Figures 24 - 29 and the data resulting from determination of each element are shown in Figures 30 - 35. The concentrations of those metal impurities in the ilmenite ore and residue after leaching as determined by the WDXRF method in this study are summarized in Table 14.

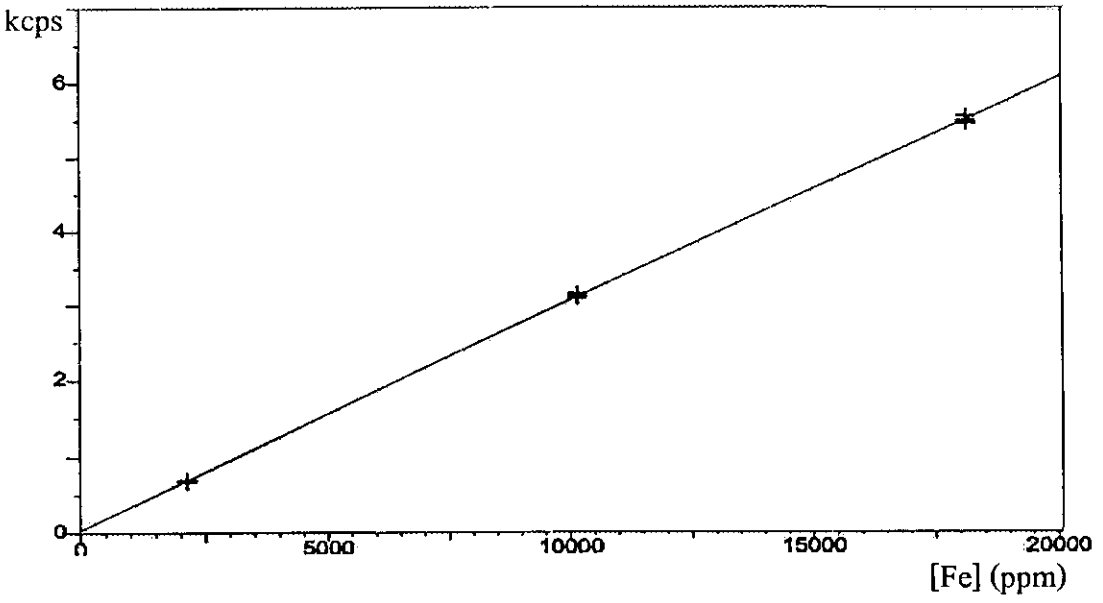

Figure 24 Calibration graph of Fe.

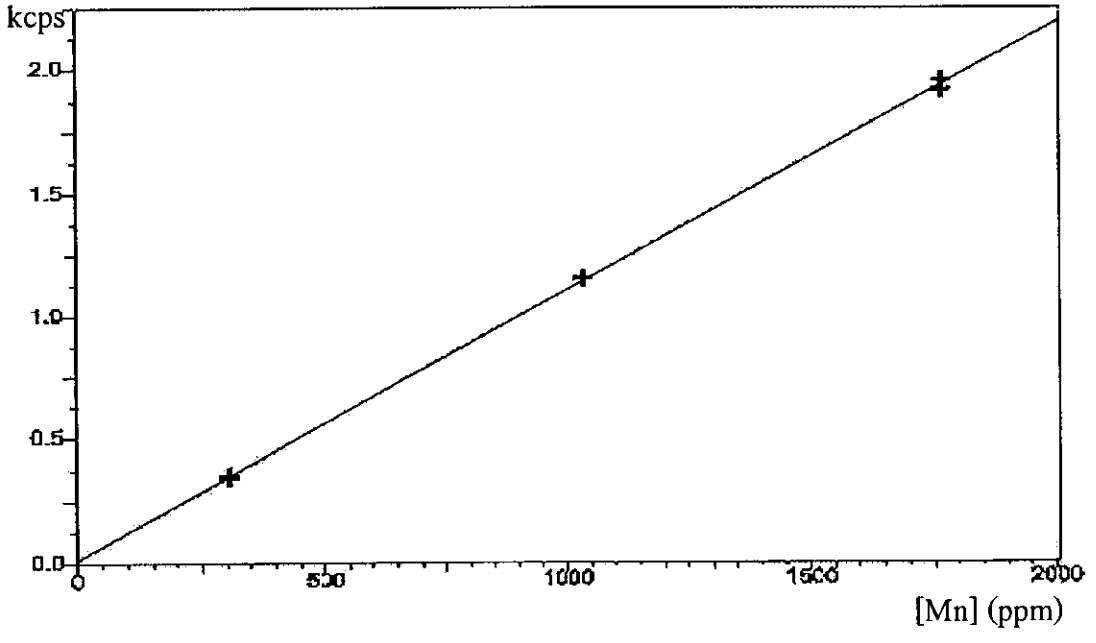

Figure 25 Calibration graph of Mn.

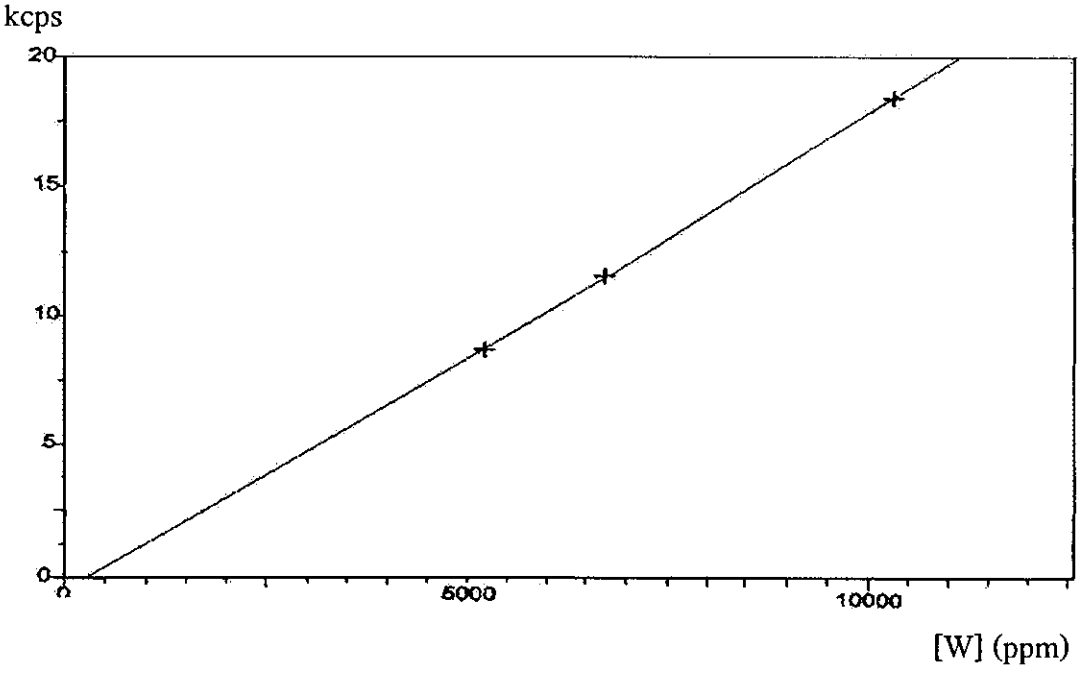

Figure 26 Calibration graph of W.

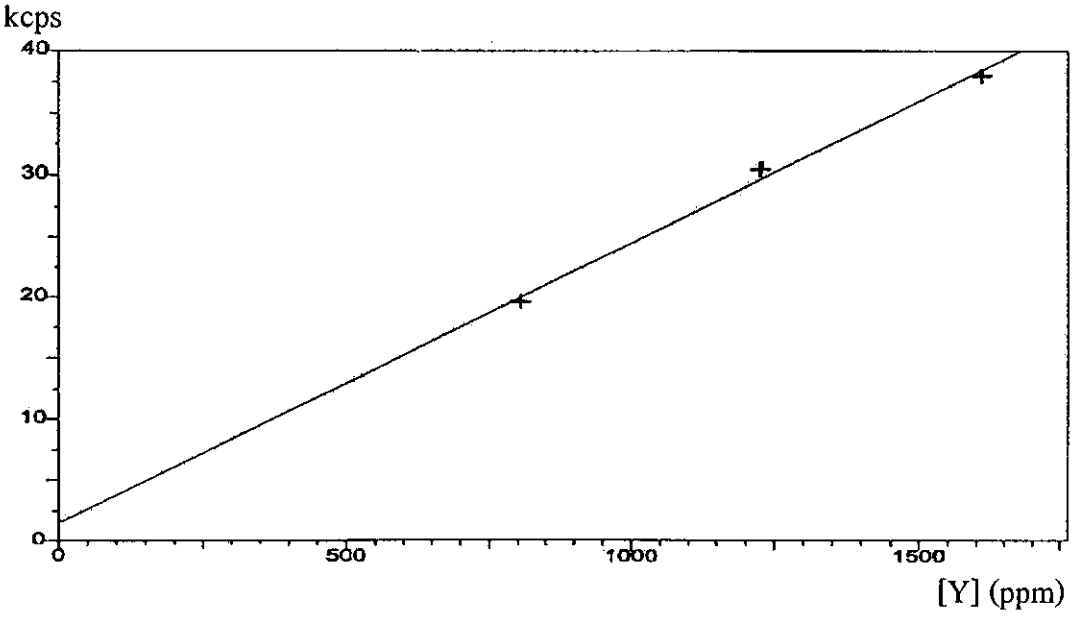

Figure 27 Calibration graph of Y.

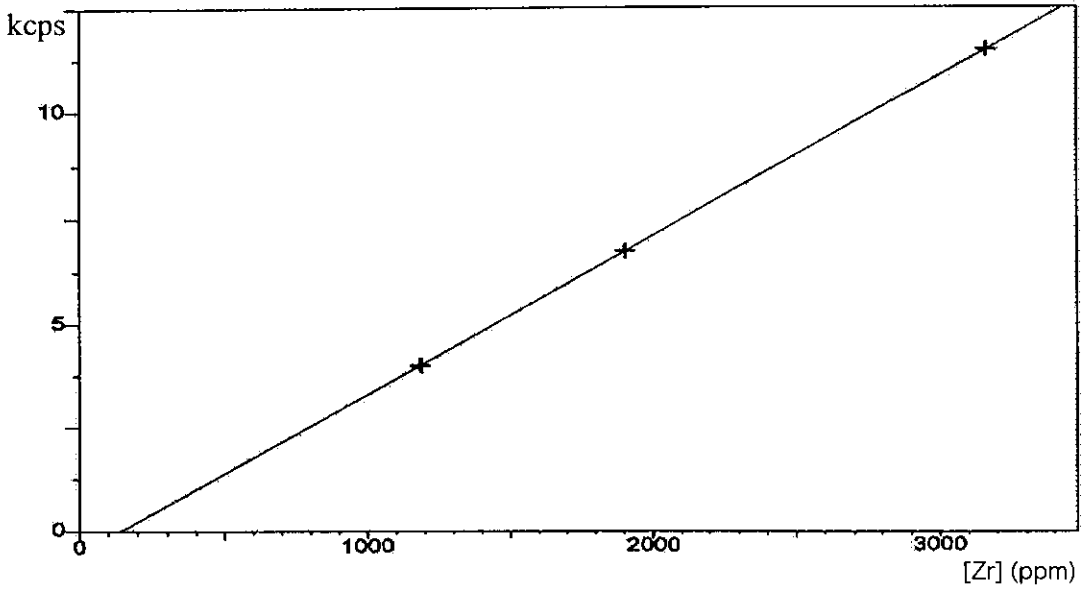

Figure 28 Calibration graph of Zr.

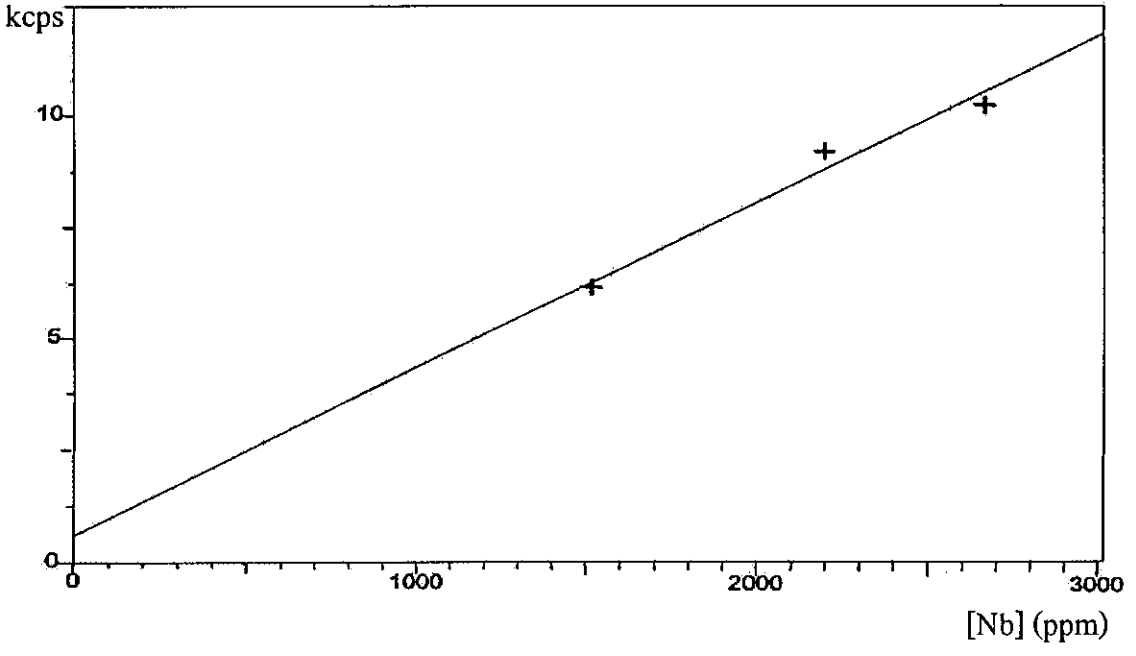

Figure 29 Calibration graph of Nb.

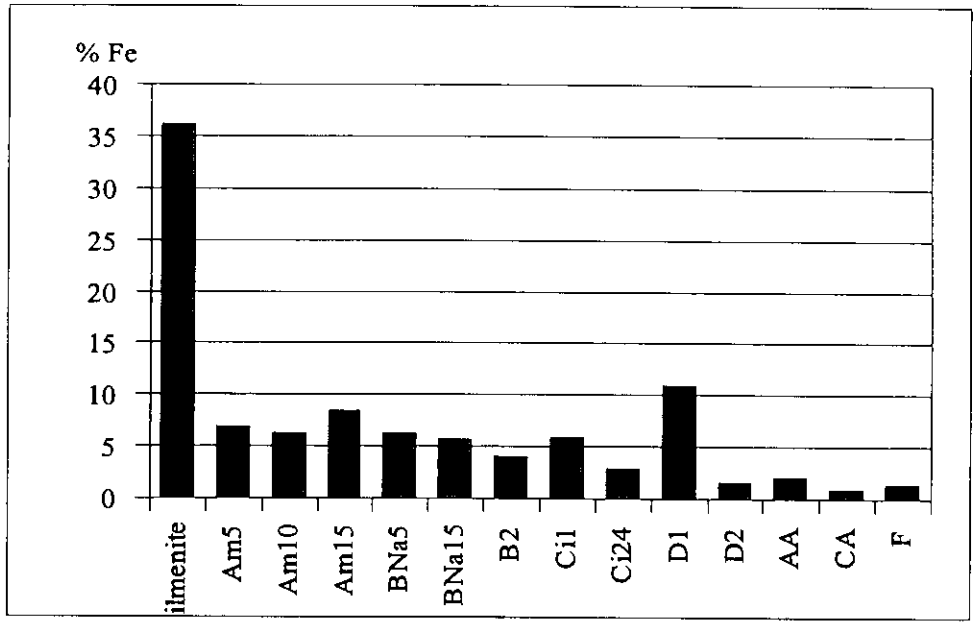

Figure 30 Data resulting from determination of Fe.

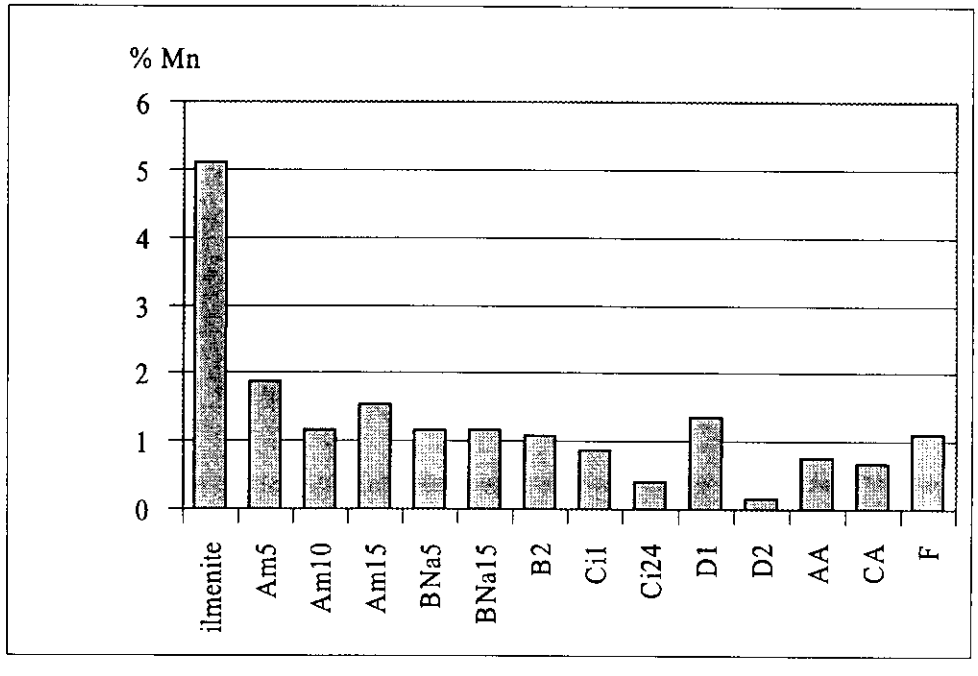

Figure 31 Data resulting from determination of Mn.

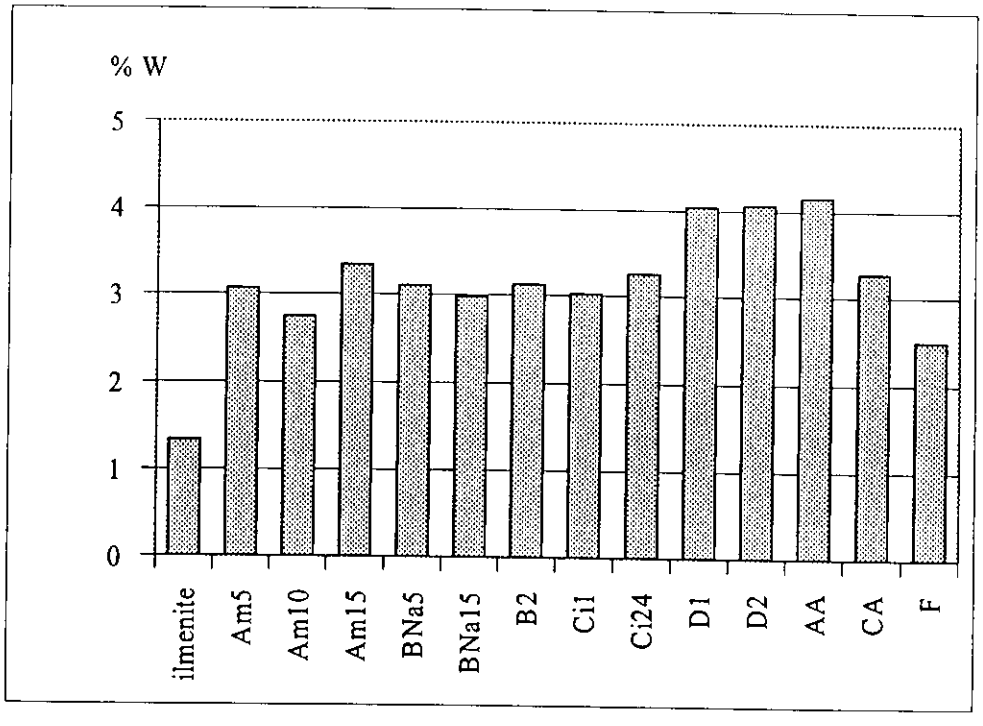

Figure 32 Data resulting from determination of W.

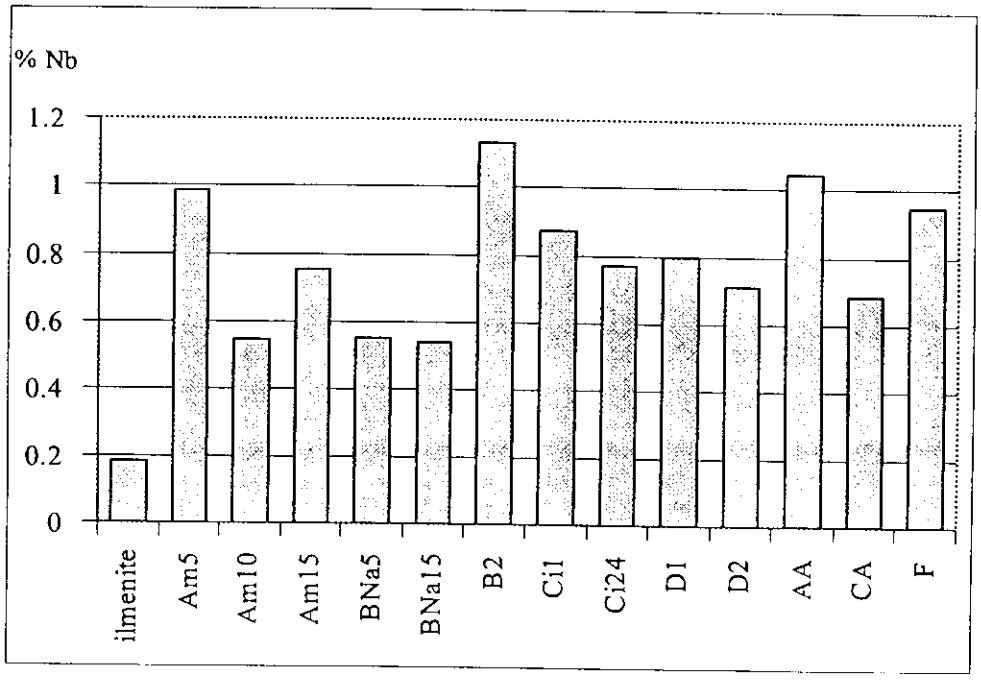

Figure 33 Data resulting from determination of Nb.

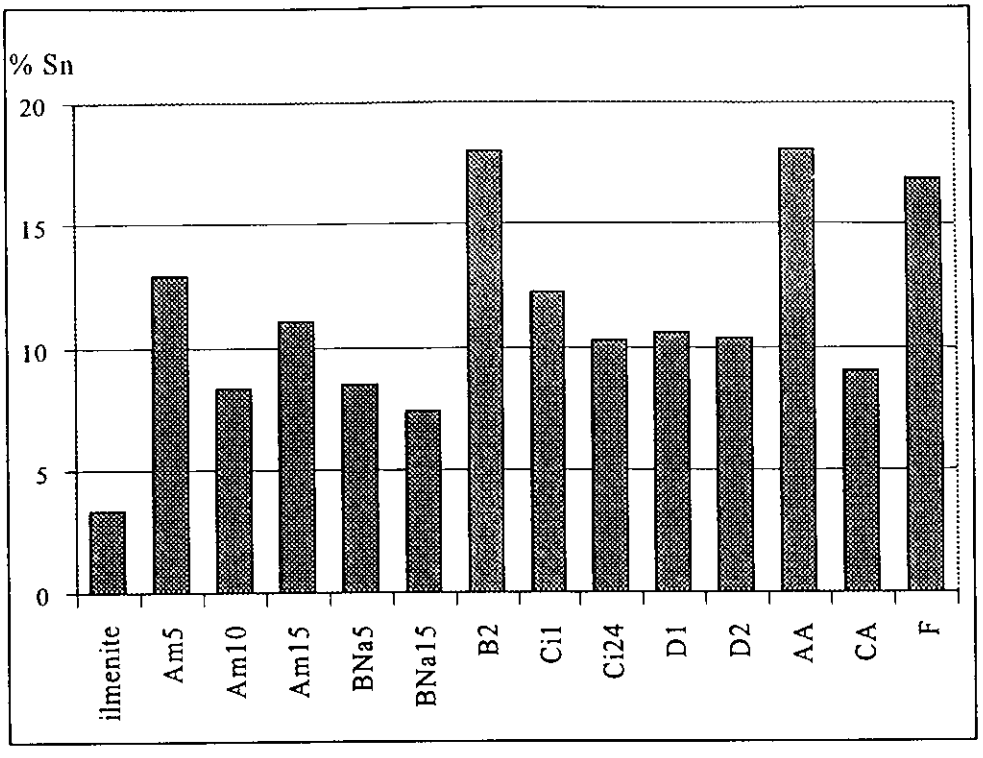

Figure 34 Data resulting from determination of Sn.

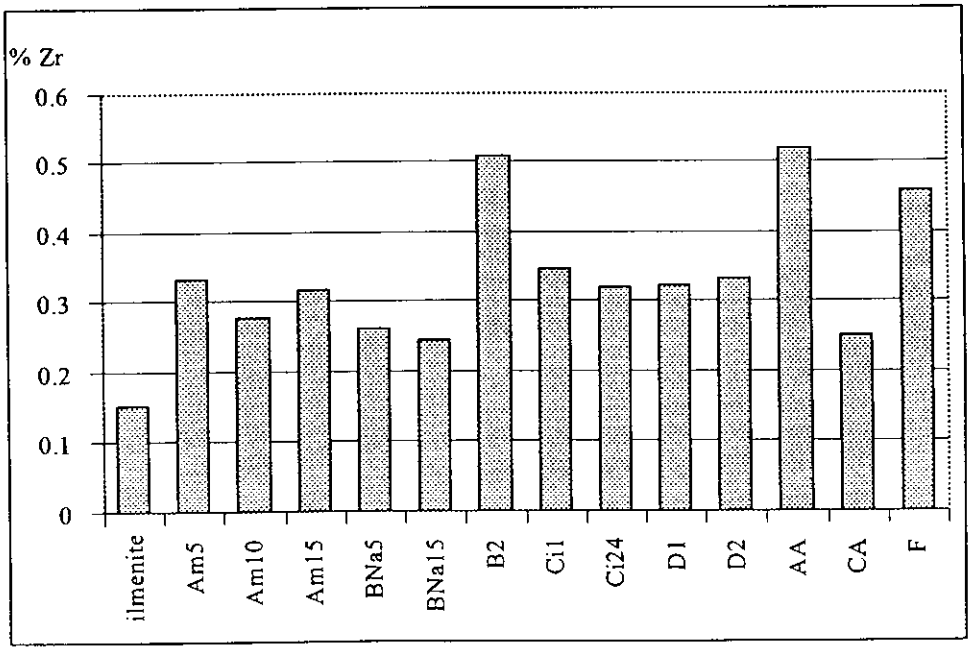

Figure 35 Data resulting from determination of Zr.

Table 14 Composition of ilmenite ore and the residue after leaching.

sample	Element (%)						
	Fe	Mn	W	Nb	Sn	Y (ppm)	Zr
ilmenite	36.10	5.10	1.34	0.18	3.33	<13.85	0.15
Am5	6.81	1.88	3.07	0.98	12.94	192.87	0.33
Am10	6.14	1.16	2.75	0.55	8.36	<13.93	0.28
Am15	8.43	1.55	3.34	0.75	11.08	<13.70	0.32
B1Na5	6.25	1.15	3.12	0.55	8.48	<13.93	0.26
B1Na15	5.70	1.16	2.99	0.54	7.36	<13.73	0.25
B2	4.00	1.08	3.14	1.13	17.99	278.97	0.51
Ci1	5.86	0.88	3.04	0.87	12.25	83.57	0.34
Ci24	2.90	0.42	3.26	0.77	10.23	<13.74	0.32
D1	10.81	1.36	4.05	0.80	10.56	28.76	0.32
D2	1.53	0.16	4.06	0.71	10.32	<13.65	0.33
AA	1.95	0.75	4.15	1.05	18.06	229.97	0.52
CA	0.88	0.69	3.28	0.68	9.06	<13.68	0.25
Fs120	1.42	1.10	2.51	0.95	16.92	251.05	0.46