



Characterization of Vanadium and other Trace Elements from North-Western Nigeria using INAA and PIXE

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ABSTRACT

Two techniques: Instrumental neutron activation analysis (INAA) and Proton induced X-ray emission (PIXE) were used to characterize geological samples collected from North-Western Nigeria; Result obtained indicated that PIXE is more proficient for the analysis of Vanadium. It was also verified from the result that elements with Q_0 above ten are better analyzed with INAA. Other elements characterized include Au, Pb, V, P, K, Ca, Ti, Cr, Mn, Mg, Al, Si, and Dy.

Keywords: INAA, PIXE, Vanadium, North-Western Nigeria

1. INTRODUCTION

Vanadium is not only a subject of scientific research lately, but has found usage in high tech automobile industries as well as semiconductors and as transistors. Chrome-vanadium steels are used in the production of springs and in transmission gears and other engine parts. Titanium-vanadium alloys are used for missile cases, jet-engine housings, and nuclear-reactor components. As a catalyst, vanadium has largely replaced platinum in the manufacture of sulfuric acid and is employed widely as a photographic developer, as a reducing agent, and as a drying agent in various paints.

Thin-film materials with 'smart' properties that react to temperature variations, electric or magnetic fields, and/or pressure variations have recently attracted a great deal of attention. Vanadium dioxide (VO_2) belongs to this family of 'smart materials' because it exhibits a semiconductor-to-metal first-order phase transition near 340 K, accompanied by an abrupt change in its resistivity and near-infrared transmission. It is also of great interest in condensed-matter physics because it is a classic strongly correlated electron system. In order to integrate vanadium dioxide into microelectronic circuits, thin-film growth of VO_2 has been studied extensively, and studies of VO_2 nanoparticles have shown that the phase transition is size-dependent [1].

Also Materials with strong electronic Coulomb interactions play an increasing role in modern materials applications. "Thermochromic" systems, that exhibit thermally induced changes in their optical response, provide a particularly interesting case. The optical switching associated with the metal-insulator transition of vanadium dioxide (VO_2), for example, has been proposed for use in "intelligent" windows that selectively filter radiative heat in hot weather conditions [2].

This work focused on determining the content and the distribution of Vanadium as well as other trace elements in North-Western by two techniques: INAA and PIXE.

2. METHODS AND MATERIALS

2.1 INAA Calculations

The equation used for the calculations in INAA using the comparator method [3].

$$\frac{R_{std}}{R_{sam}} = \frac{W_{std}(e^{-\lambda T})_{std}}{W_{sam}(e^{-\lambda T})_{sam}}$$

Where R = counting rates of standard (std) and sample (sam)

W = weight of element

T = decay time

For a stable reactor flux and when performing short irradiations, the irradiation, the decay and the counting times are normally fixed for all samples and standards such that the time dependent factor cancel out. Thus equation simplifies to:

$$C_{sam} = C_{std} \frac{W_{std} R_{sam}}{W_{sam} R_{std}}$$

Where C = concentration of element.

The possibility of using a single element as a comparator for multielement NAA is attractive, and several schemes have been devised to accomplish this. The one that has become most



widely used is called the k_o method. The equation used to calculate concentrations using this method were

$$\rho = \frac{A_{sp}}{A_{sp}^*} \cdot \frac{1}{K_o} \cdot \left(\frac{f + Q_o^*(\alpha)}{f + Q_o(\alpha)} \right) \cdot \frac{\varepsilon^*}{\varepsilon}$$

where ρ = concentration, in $\mu\text{g/g}$

A_{sp} = Specific activity of comparator element(*), or sample

f = the thermal-to-epithermal flux ratio

Q_o = the ratio of the resonance integral to thermal neutron cross section

ε = the detector efficiency

k_o = the k_o factor

α = the deviation of the epithermal flux from ideality

$A_{sp} = \frac{A_p}{SDCW}$, specific count rate

$A_p = N_p/t_m$, average count rate, with N_p as the number of counts collected in the full energy peak and t_m is the counting time;

S , D and C are the saturation, decay and measurement factor, respectively. w is the weight of the element under consideration.

2.2 PIXE Calculation

When specimens (pellet made from samples) are thick enough to stop the beam, then we have $E_f = 0$ in equation below.

$$Y(Z) = \frac{N_{av} \omega_Z b_Z t_Z \varepsilon_Z^i \Omega / 4}{A_Z} N_p C_Z \int_{E_0}^{E_f} \frac{\sigma_Z(E) T_Z(E)}{S_M(E)} dE$$

It is clear that all the matrix (M) effect (i.e., those due to proton slowing and X-ray attenuation) are contained in the integral, which we denoted by $I_Z(M)$ where M denotes the specimen (SP) or the standard (ST).

$$\frac{C_Z(SP)}{C_Z(ST)} = \frac{Y_Z(SP) I_Z(ST)}{Y_Z(ST) I_Z(SP)}$$

The standards are usually single elements or very simple compounds containing the elements of interest or their near neighbors in the chart of nuclides [4].

The major merit of this ratio method is its cancellation of instrumental factors such as solid angle, efficiency, and calibration factors for charge integration. This is especially important given the practical difficulties in obtaining accurate knowledge of the detector's lineshape and intrinsic efficiency at the low X-ray energies characteristic of the light elements that are so often the major elements in environmental specimens. It also alleviates the problems of the deteriorating accuracy with which K-shell ionization cross sections and fluorescence yields are known as the atomic number falls from $Z = 20$ to 10.

Another practical point regarding major-element analysis is that the high ionization cross sections result in very high yields of characteristic X-rays. The analyst then has a choice between working with low beam currents, often well below 1 nA, or using either collimation or a rather large specimen-detector distance in order to maintain counting rates in the range that can be handled by a Si(Li) detector system (a few thousand counts per second). The latter choice is usually preferred on account of the potential for charge measurement errors due to leakage across insulators or due to interference when working at currents well below 1 nA.

2.3 Irradiation of Standard Reference Materials and Samples

Fourteen samples were collected across North-Western Nigeria; each sample was separately crushed with a mechanical crusher, sieved, homogenized, and then divided into two equal parts. One of each part, fourteen in all, was sent to the research accelerator at Centre for Energy Research and Development (CERD), Ile-Ife, Nigeria for PIXE analysis. The other fourteen was sent to the research nuclear reactor at Centre for Energy Research and Training, Zaria, Nigeria, for INAA irradiation and analysis.

For INAA, the irradiation times were 10min respectively, in a flux of $5.0 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ thermal neutrons. The gamma spectrometry was carried out for the fourteen. It was observed that the dead time – time intervals before another signal is accepted into the detector – for the samples (sample subjected to full neutron flux) was too high, this was attributed to the activation of interfering elements aforementioned. Thus



equipped with these insights, the above methodology was then applied to fourteen prepared samples.

For PIXE, fourteen pellets were made out of the fourteen samples. Pellets are then held fast on a ladder, akin to a slide projector; each sample is irradiated and counted (for ten minutes) just as in the NAA, subsequently the spectrum obtained is stored for qualitative and quantitative calculation at a later time. Akin to NAA, the irradiation is done together with standard reference material (SRM) for relative quantitative calculation and quality control. The accelerator at Obafemi Awolowo University has four detectors; one detector for PIXE analysis, the second for Rutherford backscattering spectroscopy

(RBS), the third for particle induced gamma-ray emission analysis, and the fourth is positioned right behind Faradays' cup to detect escaped charges.

Each of the two techniques first conducted quality control evaluation and validation analysis on standard research materials SRMs. The results obtained are shown on Tables 1 and 2. For PIXE, the standard reference materials utilized for validation are NIST 278 (Obsidian rock) and BCS355 (Tin ore). These standards were irradiated with protons, thereafter analyzed for ten minutes. The elemental concentrations obtained are tabulated alongside the certified values in Table 1.

Table 1: Elemental Concentrations (ppm) in Selected Reference Materials using PIXE

Analyte	NIST 278 (Obsidian rock)		BCS 355 (Tin ore)	
	Reported value	This work	Reported value	This work
Si	341436	342392.3±9039	5000.0	5152.6±484
Cl	NA	609.1±140	NA	321.3±187
K	3453	3465.8±148	-NA	3215.6±562
Ca	7025	7057.4±114	2630	2688.5±528
Ti	1468	1475.9±30	3700	3693.7±76
Mn	403	378.8±15	NA	1795.6±39
Fe	14268	14321±72	170800	170282.8±255
Cu	5.9	6.4±7.3	850	848.8±35
Zn	55	56.4±17.3	590	589.5±32
Rb	127.5	127.8±21	-	-
Zr	NA	265.3±48	-	-
Cr	-	-	NA	60.7±25
As	-	-	1400	1398.5±50
Sn (K)	-	-	314200	314901.4±4881
Sn (LA)	-	-	314200	314969.2±1134
Ba	1140	1144.1±229	-	-
Ce	62.2	65±32	-	-
Cd	-	-	NA	1070±577
W			3500	3491.7±152

NA: Not analyzed.

For INAA, analysis of standard reference materials (SRMs), IAEA-soil-7 and Single Element (gold) standard foil (0.01396g)

were conducted for quality control and validation. The result obtained is shown alongside the certified values in Table 2.

**Table 2: Elemental Concentrations (ppm) in Selected Reference Materials using INAA Spectrometry**

Analyte	IAEA-Soil-7	This work	Gold Foil (single element standard)	
	Reported value		Reported value	This work
Antimony	1.7		1.66±1.5%	-
Arsenic	13.4		13.12±1.5%	-
Gold	-		BDL	0.01396
Mercury	0.04		0.0406±2.0%	0.01365±2.5%

BDL: Below detection limit.

Satisfied with the above validations, the samples were subjected to same experimental procedure.

The result obtained is shown below.

3. RESULT AND DISCUSSION

riddle with interferences. The result from INAA is shown on Table 3.

The result of INAA from Table 3 indicated that elements with Q_0 above ten were observed to be sufficiently activated. Their gamma spectrum, i.e. their energy peaks are

Table 3: Element Concentrations (In Ppm, Unless Otherwise Indicated) Obtained in Analyses of Gold Ores Samples

Sample	Elements concentration							
	Au, %	Mg, %	Al, %	Ca, %	Ti, %	V	Mn	Dy
Sample A	0.90±50%	0.54±0.03	2.00±0.05	BDL	BDL	4.3±1.2	3.0±0.1	BDL
Sample B	0.45±42%	0.17±0.02	1.20±0.04	BDL	BDL	BDL	0.6±0.1	BDL
Sample C	BDL	0.14±0.02	1.03±0.03	BDL	BDL	14.3±1.8	186±03	BDL
Sample D	345.6±1.5%	0.42±0.03	0.87±0.03	0.27±0.05	BDL	26.4±2.6	163±03	BDL
Sample E	7.99±8.3%	0.27±0.02	1.06±0.03	BDL	0.13±0.03	7.0±01	4.3±0.2	BDL
Sample G	487.6±1.4%	0.88±0.02	0.41±0.02	BDL	14.04±3.5	68.0±04	306±05	BDL
Sample I	BDL	0.70±0.04	2.00±0.05	BDL	BDL	BDL	2.3±0.1	BDL
Sample J	15.4±1.7	0.28±0.03	3.10±0.1	BDL	BDL	36±04	117±02	BDL
Sample K	208.9±2.1	BDL	BDL	BDL	9.70±1.3	BDL	380±06	BDL
Sample L	BDL	0.17±0.02	1.26±0.03	BDL	BDL	13±1.4	156±03	BDL
Sample M	3.8±18.2%	1.0±0.10	39.3±5.5	BDL	BDL	BDL	5.0±0.2	BDL
Sample N	473.8±1.5%	0.41±0.04	1.62±0.05	BDL	19.4±0.7	94±04	296±04	BDL
Sample P	543.9±1.5%	0.14±0.03	0.52±0.02	BDL	23.4±0.8	95±04	372±06	BDL
Sample Q	0.68%±1.1%	BDL	BDL	BDL	BDL	BDL	322±05	BDL

BDL: Below Detection Level, 0.1% = 1000ppm



Table 4 shows the Result of PIXE Analysis: Average Elemental Concentration (ppm) in the Samples

Sample	Pb	Si	P	Au	K	Ca	Ti	V	Cr	Mn
Sample A	46460.2±483	377416.5±9473	2077.8±1043	BDL	20708.1±128	289.1±66	2310.8±43	74.5±29	49.2±16	188.1±18
Sample B	15932.7±287	550391.8±9522	1586.4±730	BDL	BDL	99.9±29	235.2±19	BDL	52.3±11	BDL
Sample C	5379.9±170	394457.3±8047	2075.5±707	BDL	4525.3±55	320.2±32	819.7±23	55.4±18	403.9±17	3944.5±35
Sample D	128.2±60	582448.6±13338	BDL	1718.9±96	1274.2±68	31327.5±122	129814±206	BDL	260.8±22	6023.6±52
Sample E	50332.1±438	343277.2±8033	BDL	BDL	19458.1±111	208.2±62	2397.3±36	53±24	77.9±16	BDL
Sample G	655.5±86	341083.5±12825	BDL	BDL	1401.5±60	4581.4±57	232362.9±232	BDL	346±29	11958.6±67
Sample I	11216.7±208	365260.6±7707	1652.1±763	BDL	22414.7±110	384.9±62	2905.4±33	262±24	206.3±14	113±13
Sample J	32087.7±347	367964.5±7948	3448.4±841	BDL	15251.4±96	422.5±51	2715.1±35	104.9±25	118±16	1265.9±24
Sample K	BDL	243974.5±16249	BDL	BDL	631±68	8054±69	360244.9±288	BDL	663.1±38	20015±90
Sample L	18591.8±268	411887.3±8032	2514.6±732	BDL	10626.1±79	370±42	915.3±28	67.9±21	102.2±13	1639.8±13
Sample M	40918±393	334759.7±7867	4704.3±922	BDL	29259±129	323.5±76	3668.7±40	209.3±28	113.4±15	201.3±16
Sample N	165.2±82	539773.8±16733	BDL	532.6±85	1281±82	44195.4±141	233525.2±280	1492.5±49	290±36	14859.6±85
Sample P	BDL	358373.9±15088	BDL	10279.2±22	1511.2±71	9172.8±79	231040±	BDL	295±34	10994.2±75
Sample Q	59.2±54	169638.3±10416	BDL	BDL	681±45	8490.2±58	136234.4±164	BDL	2455.1±32	9017.9±61

BDL= Below detection level



Several adjustments have to be done before analysis could be carry out. For elements on Table 3 that have Q_0 below ten, their analyses were without complications as in the previews. Their energy peaks were minimally riddle with interference. Comparing Table 3 and 4, specifically the columns of vanadium (V), it can be deducted from sample N that PIXE is more efficacious in the analysis of vanadium. It would be prudent for Miners or corporate bodies interested in the analysis of geological samples for the characterization of vanadium to employ the services of PIXE. On the other hand, if the columns designated for gold (Au) are compared, INAA appears to be more proficient in the analysis of Au. Research nuclear reactor, NIRR-1, at Zaria, Nigeria can not characterize elemental Pb, because it is outside its analytical scope. For this short coming, it is safe to say that within the available multi-elemental analytical techniques in Nigeria, PIXE is more advantageous a technique for the analysis of geological sample.

4. CONCLUSION

From the results obtained, comparative advantages of the two techniques indicated that PIXE would be more suitable

in the analysis of geological sample. It however does not give PIXE the exclusive advantage as indicated on Tables 3 and 4.

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