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RAPID METHOD FOR DETERMINING SULPHUR AND VANADIUM IN PETROLEUM PRODUCTS BY NON-DISPERSIVE X-RAY FLUORESCENCE

R. Makhija, R.G. Draper and E. Furimsky

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RAPID METHOD FOR DETERMINING SULPHUR AND VANADIUM IN PETROLEUM PRODUCTS BY NON-DISPERSIVE X-RAY FLUORESCENCE

by

R. Makhija*, R.G. Draper** and E. Furimsky***

ABSTRACT

The presence of sulphur and vanadium in fuels is of great concern to producers and users. Sulphur levels must be controlled to meet environmental requirements while corrosion by vanadium during combustion may result in serious equipment damage.

The involvement of the Energy Research Laboratories in the development of technologies for processing of high sulphur and vanadium content crudes resulted in a need for a rapid analytical method because a great number of samples had to be analysed in a short period of time. The results are used to control technological parameters during thermal hydrocracking experiments performed in the pilot plant.

A method is described for simultaneous determination of sulphur and vanadium in petroleum products by non-dispersive X-ray fluorescence. The method is rapid, non-destructive and at least as accurate as previous wet chemistry methods. Sulphur and vanadium can be determined in the ranges of 0.1 to 5.0 per cent and 20 to 4000 parts per million, respectively. The method is suitable for all relatively homogeneous petroleum fractions and residuums, including solid pitches. Preliminary results show that titanium can be analysed in addition to sulphur and vanadium.

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*Technician, **Head, and ***Chemist, Petroleum and Gas Laboratory, Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada.

METHODE RAPIDE DE DETERMINATION DU SOUFRE ET DU VANADIUM DANS LES PRODUITS PETROLIERS PAR LA FLUORESCENCE X NON DISPERSIVE

par

R. Makhija*, R.G. Draper** and E. Furimsky***

RESUME

Les producteurs et les usagers des carburants sont préoccupés de la présence du soufre et du vanadium dans ces produits. La teneur du soufre doit être contrôlée afin de satisfaire les normes de l'environnement. D'autre part, la corrosion occasionnée par le vanadium lors de la combustion peut causer de sérieux dommages à l'équipment.

La participation des Laboratoires de recherche énergétique au développement de technologies de transformation des pétroles bruts à haute teneur de soufre et de vanadium a encouragé la création d'une méthode analytique rapide pour analyser le plus grand nombre d'échantillons possibles en peu de temps. Les résultats sont employés pour contrôler les paramètres technologiques pendant les expériences d'hydrocraquage thermique effectuées à l'usine pilote.

Dans le rapport on décrit une méthode pour déterminer simultanément la teneur du soufre et du vanadium dans les produits pétroliers à l'aide de la fluorescence X non-dispersive. Cette méthode est rapide, non-destructive et aussi précise que l'étaient les méthodes chimiques humides employées auparavant. On peut déterminer le soufre et le vanadium à l'échelle de 0.1 à 5.0 pourcent et de 20 à 4000 ppm respectivement. Cette méthode peut être appliquée à toutes les fractions et les résidus du pétrole relativement homogènes y compris le brai solide. Les résultats d'essais préliminaires ont démontré que le titane peut être analysé avec le soufre et le vanadium.

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*Technicien, **Chef et ***Chimiste, Laboratoire du pétrole et de l'essence, Laboratoires de recherche énergétique, Centre canadien de la technologie des minéraux et de l'énergie, Ministère de l'Energie, des Mines et des Ressources, Ottawa, Canada.

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INTRODUCTION

Sulphur and vanadium in petroleum fractions cause serious difficulties, especially when the fractions are used as fuels. Levels of these elements are regularly controlled during the refining of crudes and tars, such as Athabasca bitumen, which have high metal and sulphur contents. One objective of CANMET's Energy Research Laboratories is to develop a high yield process for upgrading bitumen and heavy oils. The experimental work is performed in a thermal hydrocracking pilot plant (1). More information on the concentration of various elements is required for a better understanding of the process. A rapid instrumental method to determine sulphur and vanadium simultaneously by X-ray fluorescence was thus investigated (2). This technique is currently being applied to the determination of sulphur (3). The possibility of determining titanium in addition to sulphur and vanadium was also investigated.

ANALYTICAL PROCEDURE

Instrumentation

A small compact bench-model INAX type 311 non-dispersive X-ray fluorescence analyzer of rugged construction was used (2). The radioactive source is Fe^{55} isotope (20 mCi), contained in a small radiation-proof cassette which can be changed easily and safely. This instrument can be pre-programmed for eight elements, four of which are measured at a time, the data being displayed in four solid-state display registers. Measuring the other four elements is done by flicking the program selector switch. Further elements can be determined by changing cards inserted in slots in the front panel.

Because the source is annular, a very short air path is possible, eliminating the need for vacuum operation for lighter elements such as silicon or aluminum. The INAX source assembly can be connected to a helium reservoir so that the air column through the centre of the assembly can be purged. The low mass per unit volume of the helium gas and its low atomic number eliminate the absorption problem due to air.

The detector in the analyzer is a disc of pure silicon, normally of 5-10 mm active diameter and 3-mm thickness, cooled to a very low temperature by connecting it to a rod immersed in liquid nitrogen at its other end to prevent current leakage. The detector assembly is in a vacuum to minimize

heat loss. The vacuum enclosure is secured by a thin window of beryllium which allows X-ray penetration to the detector. Steps in the operation of the instrument are described in the Appendix.

Sample Preparation

Liquid samples require no preparation. They are poured into the cell lined with 6-μm Mylar film. Viscous fuel oils are warmed before analysis to ensure homogeneity and ease of pouring. Samples are poured into the cells to a minimum depth of 5 mm - any more has no effect on results, but if the layer is too thin, inconsistent results are obtained.

On a few occasions, difficulties were experienced with settling of samples, particularly with heavier fractions left in the cell for a period of time. It is essential, therefore, that fresh samples be used.

Solid samples are ground to a fine powder - minus 200 mesh (74 μm) for coals or other crystalline samples - otherwise X-ray interference effects within the crystals can cause serious error. About 0.25-0.35 g of powdered sample is spread on the Mylar window of the cell. For solid pitch samples, sufficient toluene or benzene is added dropwise to moisten them and the solvent is removed by air or vacuum drying. This results in a homogeneous sample film in direct contact with the Mylar window.

The prepared samples are placed on the detector and measurements are made. The cells are cleaned and dried after use. A new Mylar film is used for each sample. It is important to have the correct thickness and homogeneity of the samples before measuring.

Analysis Procedure

The prepared sample is placed in the X-ray beam and gross intensities of the sulphur and vanadium k lines are measured. The count is then compared with that of a calibrated sample to give the concentration of sulphur or vanadium. To eliminate instrument variations and to ensure accuracy, each set of samples must be compared with a similar standard sample of the same substance which has been analysed by other standard methods.

Accuracy

The intensity of X-ray used for analysis is extremely small compared with that used for optical measurements. Most measurements agree with the mean value within a spread equal to the square root of that value. Accuracy is increased by using the average of at least five measurements.

Safety

The 20 mCi (740 MBq) Fe^{55} radioactive source is enclosed in a demountable radiation-proof cassette which allows safe handling and complete screening from the operator at all times. Frequent radiation measurements, directly on the source cassette or on the X-ray analyser and on the sample slide during operation, revealed radiation levels well below the limit of 0.25 milliRem/hour given by the Atomic Energy Control Board of Canada.

RESULTS AND DISCUSSION

The samples chosen for this work were from a 1-barrel-per-day hydrocracking pilot plant (1) as reactor samples, recycle oils, solid pitches, asphaltenes and other fractions. Also included were fuel oils containing low vanadium and sulphur previously analysed by conventional methods, e.g., vanadium determined by spectrophotometric method ASTM D-1548 and sulphur by both the ASTM D-129 bomb method and by the Leco method which is a modification of the ASTM D-1552 combustion method. Results obtained with the X-ray method and with standard methods are given in Tables 2 to 6.

Results for solid pitches are given in Table 2. For four different sets of samples containing 4.0 to 4.5% sulphur and 700 to 3500 ppm (mg/kg) vanadium, differences were small between results obtained by X-ray fluorescence and those obtained by conventional methods. For most samples, measured sulphur content differed by less than 0.1%, with the largest difference being 0.27%. For vanadium, the discrepancies ranged from 2 ppm to 162 ppm, with a mean of about 73. These differences are small compared with those permitted by ASTM standards.

Comparative results for recycle oils are shown in Table 3. Differences between the X-ray and standard methods were again small. Results for

reactor samples, heavy ends and asphaltenes are shown in Tables 4, 5 and 6. The differences in the results again were much less than the ASTM limits.

In Table 7, results are given for samples containing between 39 and 140 ppm (mg/kg) vanadium and sulphur between 1 and 4%. To account for interference caused by K_β titanium line the following equation must be applied to calculate the low vanadium content:

$$V\ (ppm) = 4215 \left(\frac{V}{Sc} - \frac{Ti/Sc}{5.4} - 0.0070 \right) \qquad (1)$$

where V, Ti and Sc represent the counts for vanadium, titanium and background respectively for a particular sample.

Equation 1 represents the least-squares fit of the line obtained by plotting vanadium in ppm (mg/kg) for known samples against corrected counts, $C_c = (V-Ti/5.4)/Sc$. The corrected counts take into account the overlap of K_β of Ti with K_α of V due to nearly the same energies of the radiations. The contribution of K_β can be calculated exactly from the well resolved K_α radiation of Ti through the formula:

$$K_\beta/K_\alpha = 5.4 \qquad (2)$$

The slope was found to be 4215 with an intercept of 0.0070 as shown in Fig. 1. Values of the slope and intercept vary slightly with different instruments.

For the high-vanadium-content samples, the following equation was derived by regression analysis:

$$V\ (ppm) = 11252.5\ C_c^{1.37} \qquad (3)$$

where $C_c = (V-Ti/5.4)/Sc$

Correlation of experimental and calculated results is shown in Fig. 2. Accuracy decreases as vanadium content approaches 20 ppm.

Results shown in Fig. 3 and 4 clearly indicate that the X-ray method compares favourably with the standard methods currently in use.

The method is also being used to measure levels of titanium in the same samples, the objective being simultaneous analysis of three elements - sulphur, vanadium and titanium - using the Fe^{55} radioactive source. Interim results of this phase of the work are shown in Tables 8 and 9.

CONCLUSIONS

This study indicates that, in the concentration ranges tested, the X-ray fluorescence method is suitable for quantitative analysis of sulphur and vanadium and possibly of titanium, and has definite advantages over the methods previously used, for the following reasons:

(a) Analysis time is reduced to 5 minutes per sample compared with 6-8 hours.

(b) The possibility of error is considerably reduced because the analysis is performed on the original unchanged sample.

(c) Because the method is non-destructive, the sample can be recovered unchanged after analysis.

(d) The method is more precise than others already in use.

REFERENCES

1. Merrill, W.H., Logie, R.B. and Denis, J.M. "A pilot scale investigation of thermal hydrocracking of Athabasca bitumen"; Research Report R281, Department of Energy, Mines and Resources, Ottawa, Canada; 1973.

2. Woldseth, R. "X-ray energy spectrometry"; Kevex Corporation; 1973.

3. Annual Book of ASTM Standards; 24, 575; 1976.

4. Ereiser, J. "Determination of sulphur and vanadium by INAX 311 Analyser"; Inax Report; 7; 1974.

TABLE 1

Comparison of Results Using Different Counts

Sample No.	Sulphur	Vanadium	Titanium	Background Setting
671"F"	720 ± 30	140 ± 20	141 ± 8	10,000
671"F"	7,233 ± 7	1,410 ± 56	1,464 ± 6	100,000
98-76	1,000 ± 25	4,330 ± 90	1,910 ± 40	10,000
98-76	4,990 ± 80	22,250 ± 100	9,600 ± 100	50,000
116-76	1,020 ± 25	214 ± 5	150 ± 15	10,000
116-76	2,470 ± 50	540 ± 30	370 ± 20	25,000
116-76	5,120 ± 35	1,110 ± 25	730 ± 40	250,000

TABLE 2

Comparison of Results on Solid Pitch Samples

Sample No.	Sulphur, %		Vanadium, ppm	
	X-ray	LECO	X-ray	Spectro-photometry ASTM D-1548
First set				
1	4.26	4.18	3098	3096
2	4.19	4.24	3121	3066
3	4.28	4.30	3312	3368
4	4.16	4.26	3420	3517
5	4.10	4.14	3326	3271
Second set				
6	4.13	4.08	2440	2447
7	4.11	4.08	2169	2292
8	4.09	4.12	2100	2005
9	4.06	4.09	2069	1922
Third set				
10	4.46	4.37	714	769
11	4.11	4.03	1172	1015
12	4.13	4.06	1541	1428
13	4.04	4.00	1446	1449
14	4.14	4.02	1805	1837
Fourth set				
15	4.30	4.07	1810	1854
16	4.24	4.13	1742	1713
17	4.25	4.11	1654	1571
18	4.11	4.16	1567	1667
19	4.07	4.06	1510	1588
20	4.45	4.26	1680	1664
21	4.08	4.23	1770	1932
22	4.48	4.21	1800	1883
23	4.29	4.27	1591	1615
24	4.16	4.00	1661	1771

TABLE 3

Comparison of Results on Recycle Oils

Sample No.	Sulphur, %		Vanadium, ppm	
	X-ray	Bomb ASTM D-129	X-ray	Spectro-photometry ASTM D-1548
First set				
1	3.69	3.72	877	811
2	3.84	3.83	753	---
3	3.82	3.87	785	734
4	3,80	3.80	690	---
5	3.82	3.70	792	746
6	3.77	3.35	730	618
7	3.72	3.75	785	744
8	3.74	-----	748	---
9	3.68	-----	714	---
Second set				
10	3.66	3.62	1178	1274
11	3.65	3.60	1043	1047
12	3.66	3.63	939	928
13	3.53	3.55	986	914
14	3.64	-----	825	---
15	3.52	-----	1011	---

TABLE 4

Comparison of Results on Residual Fuel Oil Samples

Sample No.	Vanadium, ppm		
	X-ray	Calculated	Spectro-photometry ASTM D-1548
1	-	267	270
2	295	297	303
3	290	290	295
4	288	288	293
5	228	216	212
6	246	233	234
7	247	239	248
8	302	303	300
9	285	284	293
10	256	250	254
11	203	189	171
12	288	287	279
13	374	355	385
14	386	370	374
15	382	364	389
16	368	350	359
17	368	349	366
18	365	345	348
19	363	342	344
20	346	327	334
21	428	411	412
22	393	377	370
23	231	205	191
24	-	47	23
25	-	103	105
26	-	170	173
27	-	92	88

TABLE 5

Comparison of Results on Reactor Samples

Sample No.	Sulphur, %		Vanadium, ppm	
	X-ray	Bomb ASTM D-129	X-ray	Spectro-photometry ASTM D-1548
1	4.87	4.87	-	-
2	4.20	4.10	2354	2291
3	4.00	4.06	1495	1451
4	3.98	3.79	1251	1288
5	3.77	3.78	1008	1032
6	3.96	3.91	1283	1318
7	3.80	3.84	1056	1060
8	3.98	3.96	1258	1340
9	3.78	3.77	1118	1356
10	4.05	3.99	925	827
11	3.97	4.09	4096	4027
12	3.78	3.80	2531	2592
13	4.02	4.13	4111	4095

TABLE 6

Results on Asphaltene Samples
for Sulphur, Titanium and Vanadium

Sample No.	Sulphur		Titanium, ppm	Vanadium, ppm
	X-ray	LECO	X-ray	X-ray
1	7.90	7.72	3756	816
2	7.18	6.88	3957	1117
3	8.68	8.67	1664	743
4	7.80	7.45	3574	995
5	6.59	6.71	1002	726

TABLE 7

Comparison of Results on Samples Containing Low Vanadium

Sample No.	Sulphur, %		Vanadium, ppm	
	X-ray	Bomb ASTM D-129	X-ray	Spectro-photometry ASTM D-1548
1	3.92	3.90	61	58
2	3.30	3.20	111	124
3	3.47	3.31	108	119
4	2.95	2.98	69	66
5	3.38	3.34	67	61
6	3.74	3.78	92	96
7	3.48	3.45	49	44
8	3.37	3.39	43	---
9	3.29	3.24	45	---
10	3.26	3.35	128	140
11	3.20	3.23	47	39
12	2.78	2.81	64	63
13			79	79
14	1.83	1.78	20	---
15	1.00	----	17	---
16	3.16	3.20	114	---
17	3.47	3.42	107	---
18	3.33	3.35	119	---
19	3.07	3.07	82	---

TABLE 8

Results on Solid Pitch Samples for Titanium

Sample Number	Titanium, ppm	
	X-ray	Atomic Absorption
First set		
1	3982	-
2	4170	-
3	-	4360
4	4409	-
5	4466	4550
Second set		
6	-	2869
7	2738	-
8	2884	-
9	2914	-
Third set		
10	643	-
11	2434	-
12	3605	-
13	3318	-
14	3794	-
Fourth set		
15	3565	-
16	3298	-
17	3065	-
18	2842	-
19	3133	-
20	3212	-
21	3261	-
22	2985	-
23	3367	-
24	3044	-
Fifth set		
25	3423	-
26	3194	-
27	3303	-
28	3389	3522

Sample No. 6 was used to calculate the above results.

TABLE 9

Results on Reactor Samples
for Titanium

Sample Number	Titanium ppm X-ray
1	1959
2	1925
3	2001
4	2141
5	2010
6	1809
7	2115
8	2066
9	1812
10	2205
11	2108
12	1718
13	1877*
14	1833

* Sample No. 13 was estimated by atomic absorption and used to calculate the above results by equation 2.

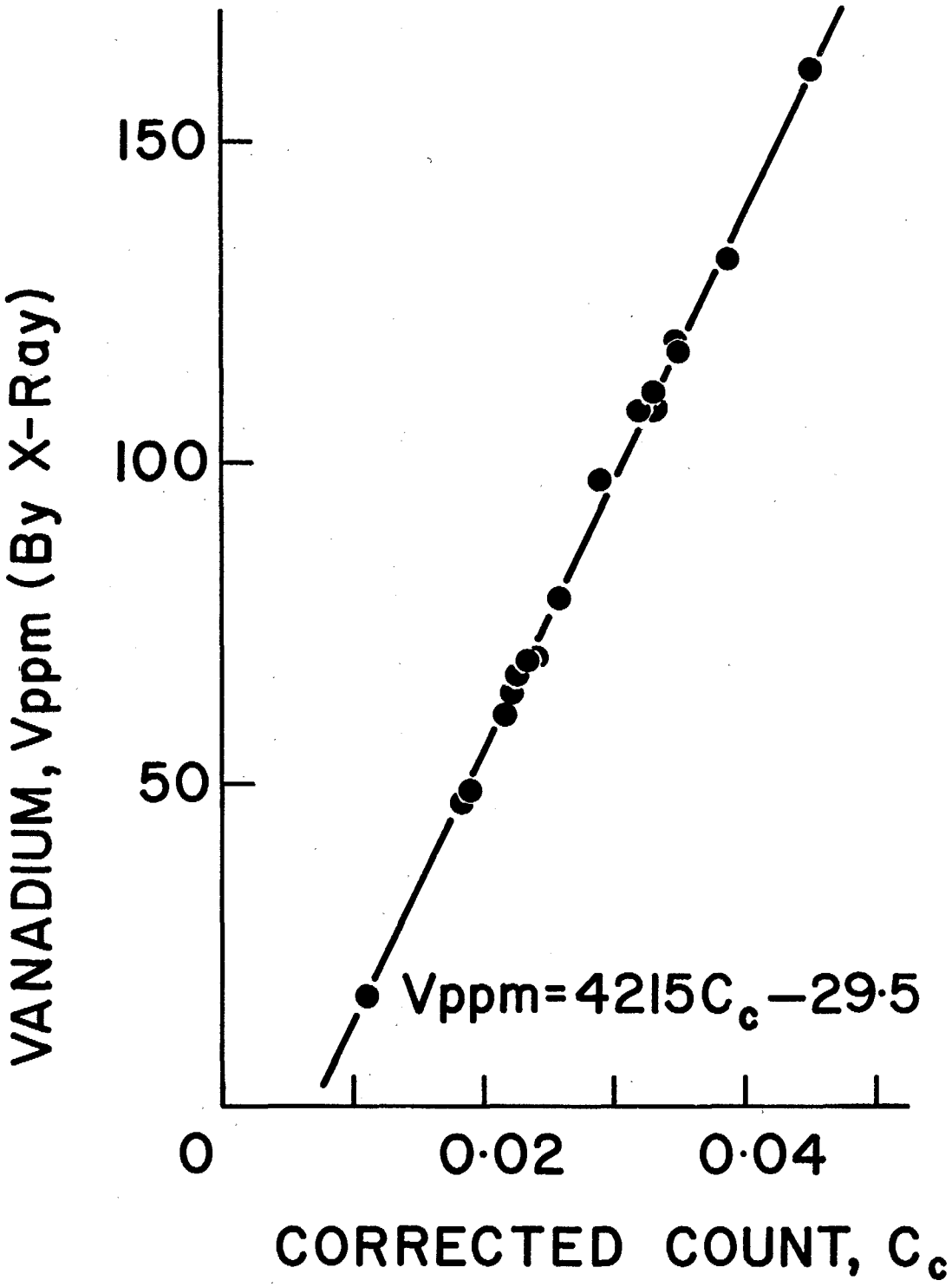

FIGURE 1 - Correlation between X-ray and Standard Methods for Low Vanadium Samples

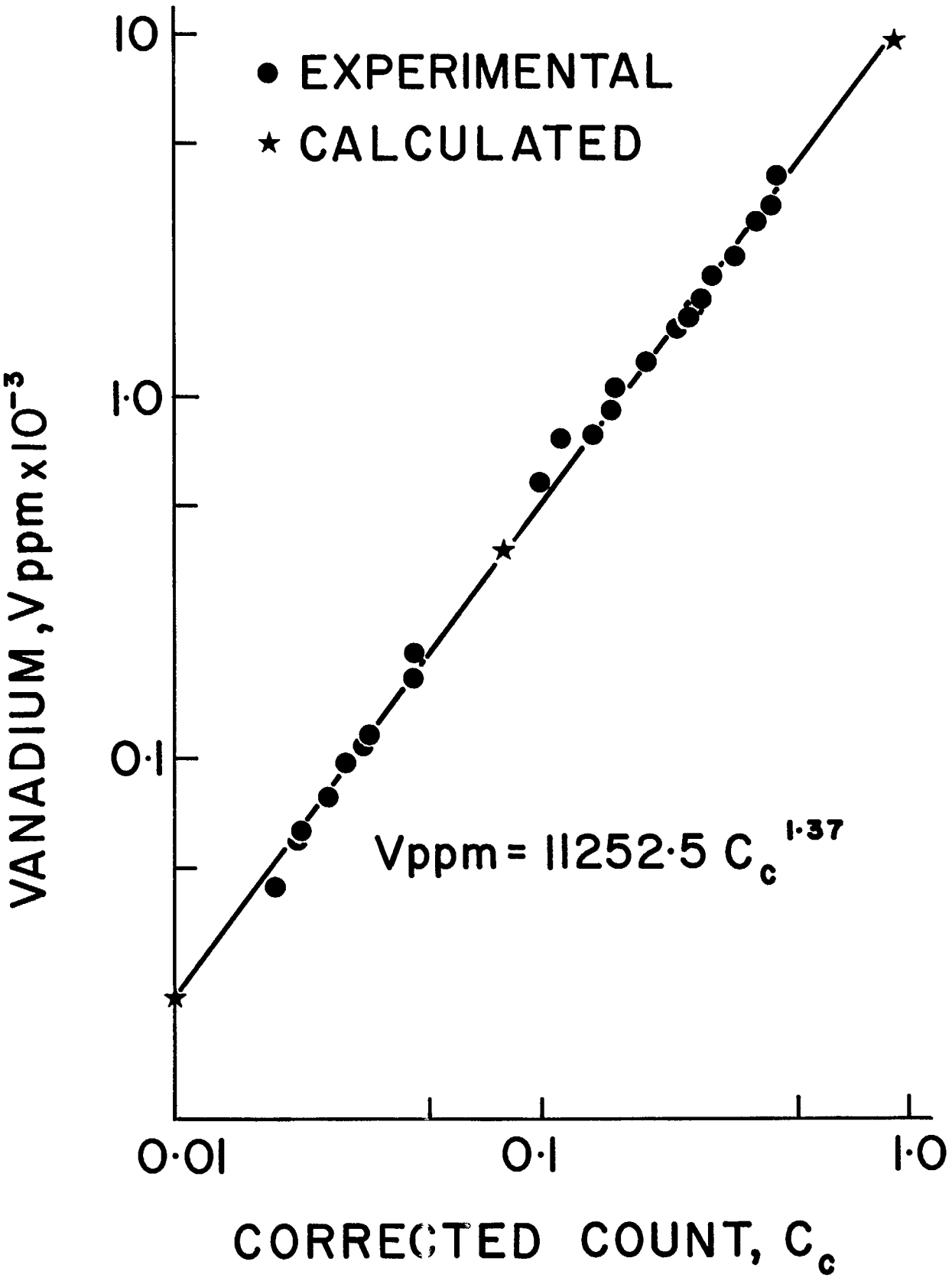

FIGURE 2 - Correlation between Experimental and Calculated Results for High Vanadium Samples

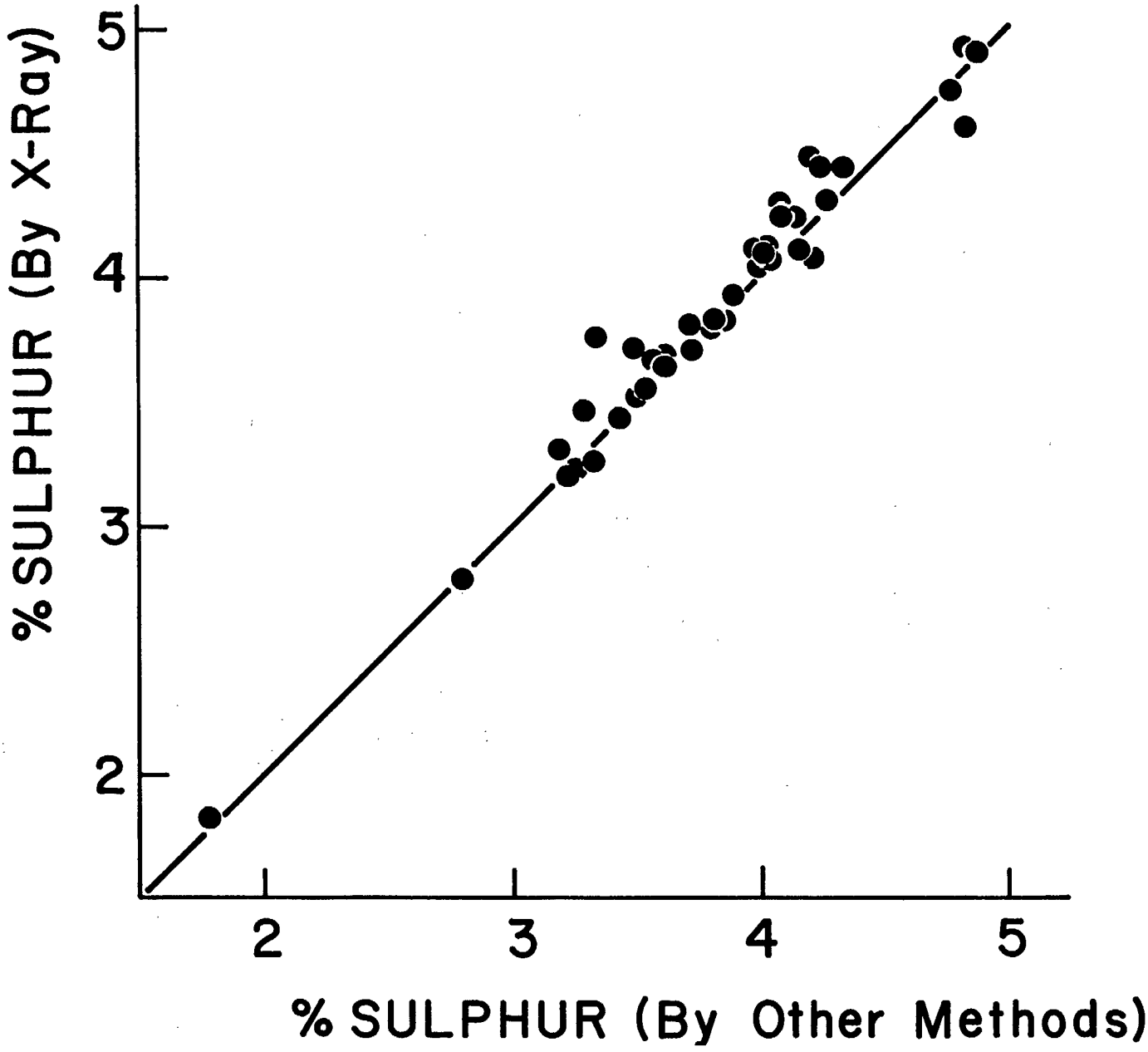

FIGURE 3 - Comparison of Sulphur Concentration (Weight Per Cent) Between X-ray and Other Method

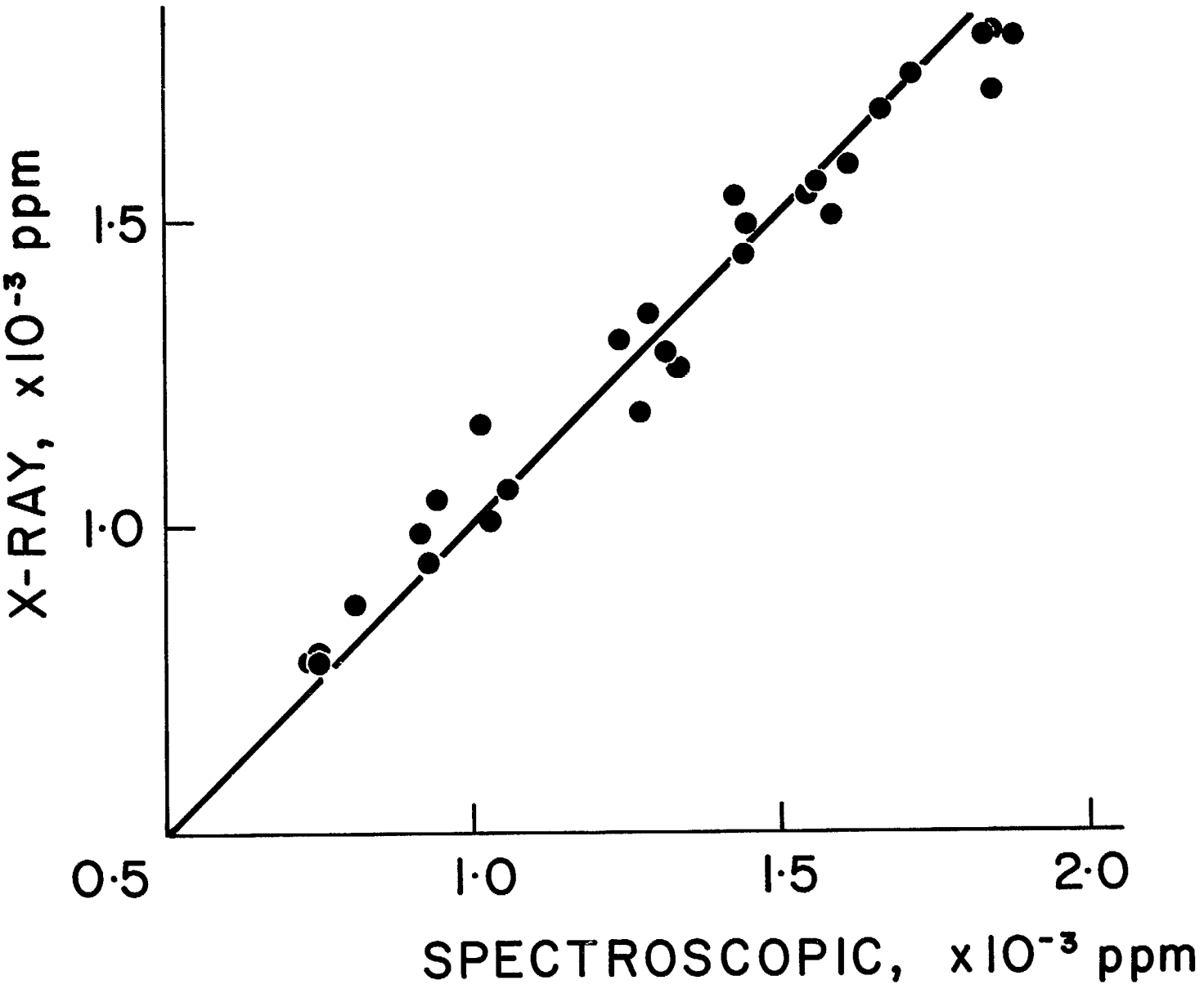

FIGURE 4 - Comparison of Vanadium Concentration (ppm) Between X-ray and Spectroscopic Methods

APPENDIX

Operation of the INAX 311 Analyser

The instrument requires only a 110 volt electrical supply and liquid nitrogen coolant to be ready for immediate operation:

(1) Turn switch on the shaping amplifier to desired range, e.g., 0-30 kev for 4 channels/kev.

(2) Set switch on the encoder program selector to A or B (A for calibration, B for sulphur, vanadium and titanium).

(3) Set the desired measurement counts on the scaler-timer thumbwheels and with the preset input switch set to PRE-SET count position, press PRE-SET, then START. For pre-set background count, the thumbwheel is pre-scaled to 1000, e.g., a thumbwheel setting of 100.0 represents a background scatter of 100,000 which is displayed in encoder channel 4. For pre-set, direct reading is in seconds whereas the encoder time display is in tenths of a second. For low sulphur and vanadium, set the thumbwheel at 25.0 or 50.0 and for high contents set it at 10.0.

(4) When the pre-set count has been reached, the counts for each of the regions of integration and encoder counting period will be displayed.

Encoder Calibration

(1) Set encoder program selector to A or B (cards) and insert the appropriate pre-programmed window card.

(2) Place a sample containing elements suitable for calibration on the detector, press RESET and START. Note the counts recorded for some short period of counting.

(3) Adjust the recessed screw (gain trim) appropriate to the range of interest on the shaping amplifier to maximize the counts in the region of interest for a given counting period.

Notes: (a) The detector rod must be cooled with liquid nitrogen.

(b) The whole detector assembly must be in a vacuum.

(c) The liquid nitrogen supply must be topped up on a regular weekly basis as detector damage will result if the dewar flask is allowed to run dry. This applies also for periods when the instrument is not being used.

For routine work in the Analytical Section, the following settings are made on the instrument:

Integration Range	0-15 kev	
Region 1	Channels 17-20	sulphur
Region 2	Channels 34-38	titanium
Region 3	Channels 38-42	vanadium
Region 4	Channels 42-55	backscatter

Depending on the sulphur and vanadium contents, 10,000 or 50,000 counts can be used. Results of a comparative study using different numbers of counts are given in Table 1.

There is no statistical difference between results obtained at 10,000, 25,000 or 100,000 background counts. Hence, 10,000 background counts can be used without sacrificing accuracy, thus saving considerable time.

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77-63 Antimony Ore CD-1: Its characterization and preparation for use as a Certified Reference Material; G.H. Faye, W.S. Bowman and R. Sutarno;
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78-2 Revision of recommended values for reference ores MP-1 and KC-1; G.H. Faye and W.S. Bowman;
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