

BR 6600849



**DEVELOPMENT OF A QUANTITATIVE METHOD FOR TRACE ELEMENT  
DETERMINATION IN ORES BY XRF:  
AN APPLICATION TO PHOSPHORITE FROM OLINDA (PE), BRAZIL.**

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**PUBLICAÇÃO IEA 413  
CEQ 58**

**MARÇO/1976**

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APROVADO PARA PUBLICAÇÃO EM DEZEMBRO/1975

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**DEVELOPMENT OF A QUANTITATIVE METHOD FOR TRACE ELEMENT  
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**ABSTRACT**

A quantitative analytical method by means of X-Ray Fluorescence intended to determine Zn, Cu and Ni trace amounts in a phosphorite ore from Olinda, PE, Brazil, was established.

Several reasons led us to choose the double dilution method with borax as the melting flux.

~~Previous studies indicated that ores diluted in borax in the form of melted samples show considerable matrix effects with respect to the element to be analysed. Later, it was possible to identify the elements already present in the ore that caused interference in the Zn, Cu and Ni determinations. Such elements were Ca and Fe and their quantities were subsequently determined.~~

The addition of appropriate quantities of Fe and Ca to standards allowed us to minimize the matrix effects without the undesired introduction of extraneous elements in the ore. Moreover, the urge of knowing the exact amounts of Fe and Cu present in the ore drove us towards a simultaneous development of another analytical method suitable to measure medium to high contents. This method also made use of the technique of dilution with melting.

Both methods present several advantages when compared to the usual ones, ~~and the following are worth mentioning:~~

- a quantitative analysis with great reproducibility of results is possible
- it is possible to extend the method to routine determinations
- in principle, it is applicable to all kinds of ores as well as other types of materials
- The main sources of error can be controlled, allowing an accuracy as high as  $\pm 1$  ppm for Cu,  $\pm 4$  ppm for Ni,  $\pm 6$  ppm for Zn and  $\pm 1\%$  for both Fe and Ca under the most unfavorable conditions.

**MAIN PURPOSE**

Among the usual methods developed for chemical analysis, X-ray techniques are remarkably advantageous if compared to any existent counterparts, mainly because of its sensitivity, velocity and resolution, specially when complex materials associated to nuclear energy processes are being investigated.

Making use of the available facilities at IEA's X-ray laboratories (at the CEQ -- Chemical Engineering Division) which include a semi-automatic single-channel Rigaku spectrometer, a variety of analytical X-ray fluorescence methods were proposed to be developed.

The present work deals with the quantitative determination of trace elements in a phosphorite ore from Olinda, a town located in the Northeast region of the country. Phosphorite was our choice for being a

rather important ore, but also because it is a multicomponent mixture with a considerable degree of complexity, thus raising our interest in establishing a routine trace-element analytical method by X-ray fluorescence

Phosphorite is important mainly for superphosphate production, but its importance lies also on its low uranium content<sup>(2)</sup> which can well be recovered as a by product by means of chemical extraction with phosphoric acid

Our intention was the development of a practical and efficient method that could be applicable to the analysis of a great number of samples. Samples were prepared by the fusion/dilution technique because:

- Fusion methods range from simple to complex procedures
- Fusion methods do not require the rigid observance of procedural techniques, which characterizes powder methods and they also permit extension of usable analytical range.
- Dilution in a flux reduces enhancement and absorption effects<sup>(5,8,11)</sup>
- It is possible to reduce such effects still a little further by adding a highly absorbent element for those to be determined
- It is a common technique used in quantitative X-ray fluorescence analysis to reduce matrix effects and presents a more uniform sample to the X-ray beam

The experimental procedure was planned to be executed into three major steps:

#### STEP 1:

"Borax Melts" preparation with variable ore percentage relative to the flux. With these sample-pellets, besides determining optimum sample preparation conditions it is possible to determine the matrix effect upon the ore and establish the convenient sample-flux proportion in a way such that a certain detectable amount of the elements to be analysed is present

#### STEP 2:

Standard pellets preparation with the same flux and the same conditions used in step 1; confrontation between standard and sample pellets and subsequent correction of matrix-effects upon sample and standards

#### STEP 3:

Once matrix-effects upon standard pellets and sample pellets are confronted, a comparative X-ray fluorescence method is ready to be employed in order to determine the amounts of the desired elements, provided the calibration curves are constructed.

### EXPERIMENTAL PROCEDURE

The experimental procedure as outlined before in this article will be given in full detail for each step:

#### STEP 1:

As already mentioned, this step concerns:

- a) "borax melt" preparation
- b) matrix effect and detectability check out

#### a) "borax melt" preparation

Many researchers<sup>(3, 4, 6, 9, 17, 18)</sup> have attempted to determine the best melting pellet preparation conditions by employing several types of flux, but borax ( $\text{Na}_2\text{B}_4\text{O}_7$  or  $\text{Li}_2\text{B}_4\text{O}_7$ ) and an oxidizing medium ( $\text{BaO}_2$ ,  $\text{KClO}_3$ ) or an oxidation catalyst ( $\text{MnO}_2$ ) into a graphite or platinum crucible seems to be the most suitable combination mentioned in the literature

In our case, borax was chosen as the flux. However when we attempted to use a platinum crucible at an early stage of our work we found it quite inadequate because the resultant solid solution invariably adhered to the recipient thus hindering its removal.

With the acquisition of a special crucible basically a Pt-Au alloy the obtaining of a non-adherent solution became feasible. The sample thus formed proved to be ideally shaped for our analysis, as well as so transparent and so smooth at the surface that it could be immediately placed in our X-ray fluorescence apparatus to be analysed.

The ideal pellet was obtained by annealing at  $950^\circ\text{C}$  during a time interval ranging between 15 and 60 minutes, the exact value depending on the type and proportion of the sample diluted in the borax flux.

#### b) Matrix-effect and Detectability Check-Out

Once optimum pellet preparation was set we tried to obtain the best possible pellets for the phosphorite ore, aiming Zn, Ni and Cu trace analysis.

Six sample pellets were prepared at first, at different ore/flux proportions (25, 50, 100, 200, 300 and 400 mg ore with 3 g borax) in order to devise the ideal proportion and compare matrix effects in the analysis of the desired elements.

A comparison of matrix effects was made by plotting the  $K_{\alpha}$  line profile for each element for all pellets including the blank one, i.e. the one prepared exclusively with borax. Figure 1 shows Zn profiles correspondent to a blank pellet and sample pellets with 200 and 400 mg ore; both pellets show sufficient detectability with respect to Zn as can be seen by its peak to background difference, although a considerable matrix effect is observed for Ni and Cu. After extensive and careful preliminary experiments we decided to use the 400 mg ore pellet.

#### STEP 2:

According to our initial scheme, step 2 consists of standard sample preparation and minimization of the matrix effects already known to exist in our particular case.

A standard pellet containing 40  $\mu\text{g}$  Zn was initially prepared. The  $\text{ZnK}_{\alpha}$  profiles obtained with this standard when compared to the blank and sample pellet ones show the existent matrix effect (figure 2) once their respective backgrounds are obviously different. As a consequence, preparation of a blank-pellet and a sample-pellet with the same backgrounds seems mandatory.

Matrix effects are usually minimized by adding a highly absorbant compound for those to be analysed<sup>(1, 10, 14)</sup>, such as  $\text{BaO}_2$  or  $\text{BaSO}_4$  or  $\text{La}_2\text{O}_3$ .

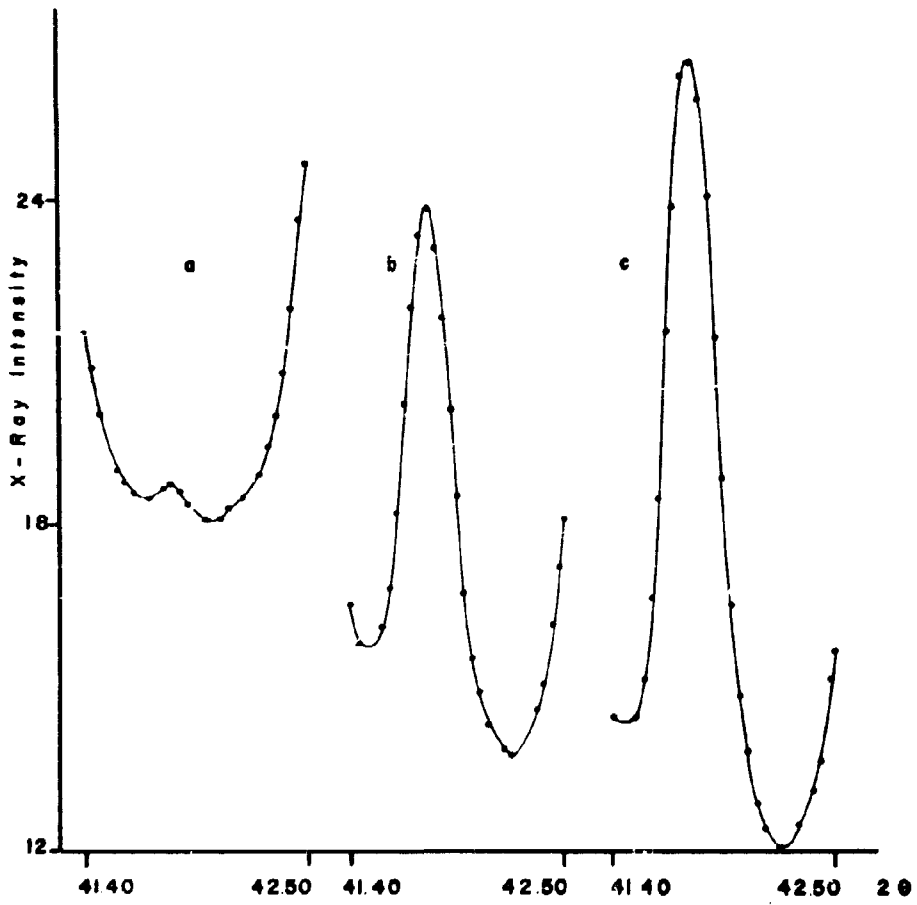


Figure 1 - Step by step scanning profile for Zn from blank pellet (a) and sample pellets with 200 and 400 mg phosphorite content (b) and (c). Differences in background heights show a considerable matrix effect is present.

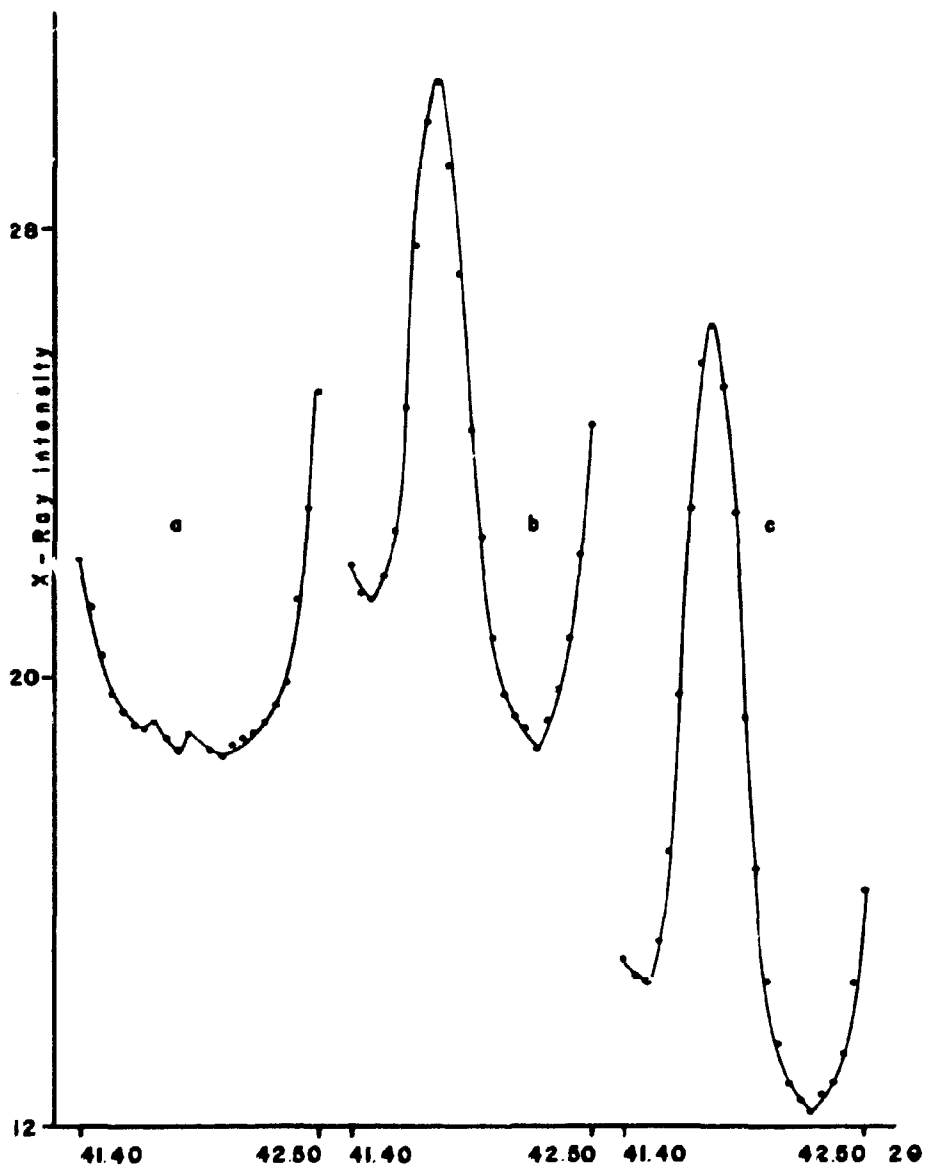


Figure 2 - Step-by-step scanning profile for Zn from blank-pellet (a) and standard-pellet with 400  $\mu\text{g}$  Zn content (b) and sample pellet with 400 mg phosphorite content (c) Differences in background heights show a considerable matrix effect is present.



As we intended to determine the exact amounts of those elements present in the phosphorite ore that interfere with the analysis of the desired elements, we undertook a meticulous search to find the main elements already present in the ore that absorb Cu, Ni and Zn radiation

This way, an unnecessary addition of an extraneous highly absorbent compound was avoided. Our investigation indicated Ca and Fe were the sought for elements, as attested by the absorption coefficient curve as a function of the wavelength  $\lambda$  (figure 3) obtained with data from the International Tables for X ray Crystallography<sup>(7)</sup>

As we needed to know the Ca and Fe quantities present in our phosphorite ore, an appropriate analytical method for medium to high concentrations was developed separately. The method developed (double dilution) for this purpose also followed rigorously the four steps already discussed, yielding the values listed below

Fe (27.2 ± 3)%

Ca (3.3 ± 1)%

With these data in mind we were able to prepare new standard pellets by adding Ca and Fe, aiming the correction of matrix effects upon Zn, Ni and Cu

Characteristic Zn, Ni and Cu  $K_{\alpha}$  profiles measured for new standard pellets presented basically the same background (figures 4 and 5) demonstrating matrix effect elimination almost entirely by Ca and Fe addition

### STEP 3:

Once step 2 was finished, step 3 was initiated. Experimental data were acquired under instrumental operation conditions given in Table I for each element analysed

Table I  
Instrumental Operation Conditions  
(Rigaku single channel spectrometer)

Element	Zn	Ni	Cu
tube voltage (kV)	45	40	40
tube current (mA)	30	30	30
crystal analyser	LiF (200)	LiF (200)	LiF (200)
target	W	W	Cr
angular position (2 $\theta$ )	41.81	48.64	45.02
Base line (V)	4.6	2.7	4.1
channel width (V)	4.8	4.8	4.8
counter	scintillation	scintillation	scintillation

Intensities of the characteristic  $K_{\alpha}$  lines for Zn, Ni and Cu at respective peak's maxima and correspondent backgrounds (blank pellet count rate) were obtained and the difference between them was taken ("net counts"). Results are presented in Table II

The Zn, Ni and Cu contents were determined by interpolating into calibration curves based on standard pellets data. These were constructed with the aid of the "least-squares" method. Uncertainties for each determination were calculated using the correspondent equations (for each curve), and the following values are the ones we finally arrived at:

**Table II**

Characteristic Zn, Ni and Cu K $\alpha$  line intensities minus  
Background intensities at peaks' maxima

Pellets	Zn		Pellets	Ni		Pellets	Cu	
	Zn K $\alpha$ net count	Zn content ( $\mu$ g)		Ni K $\alpha$ net count	Ni content ( $\mu$ g)		Cu K $\alpha$ net count	Cu content ( $\mu$ g)
std 1	227 514	1835 7	std 1	4 933	43 2	std 1	502	14 4
std 2	5 224	52 2	std 2	15 953	141 4	std 2	3 628	98 2
std 3	4 606	48 2	std 3	12 199	99 0	std 3	1 118	33 5
std 4	11 883	112 4	std 4	27 997	251 5	std 4	11 763	312 3
std 5	20 455	160 0	std 5	27 216	247 5	std 5	10 087	267 6
std 6	5 618	64 0	sample		unknown	sample		unknown
std 7	14 291	120 0	(400mg ore)			(400mg ore)		
std 8	3 405	41 0						
std 9	15 887	132 5						
sample (400mg ore)		unknown						

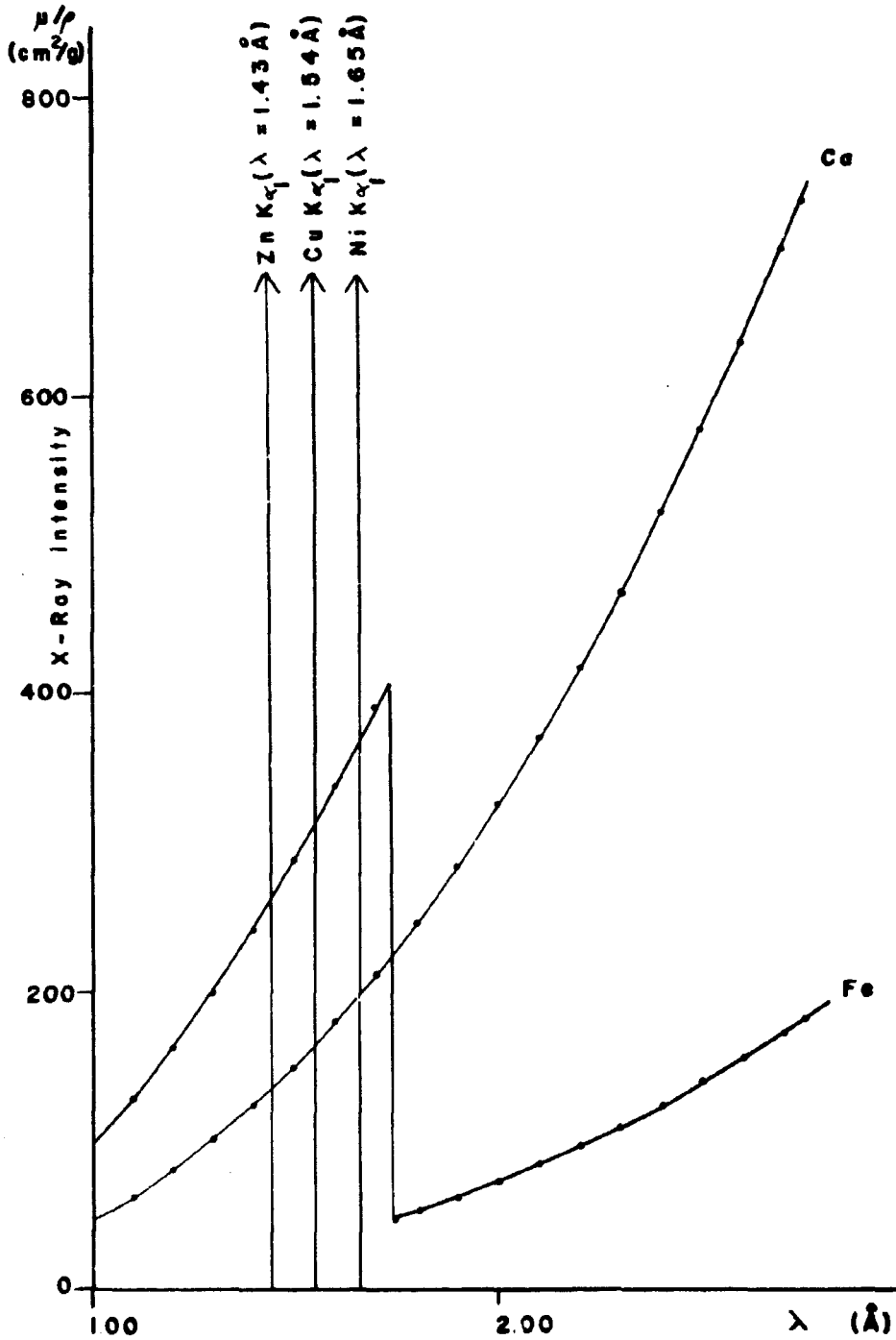


Figure 3—Absorption coefficient vs wavelength curve shows interferences caused by Ca and Fe on Zn, Cu and Ni K lines. Data from International Tables for X-Ray Crystallography.

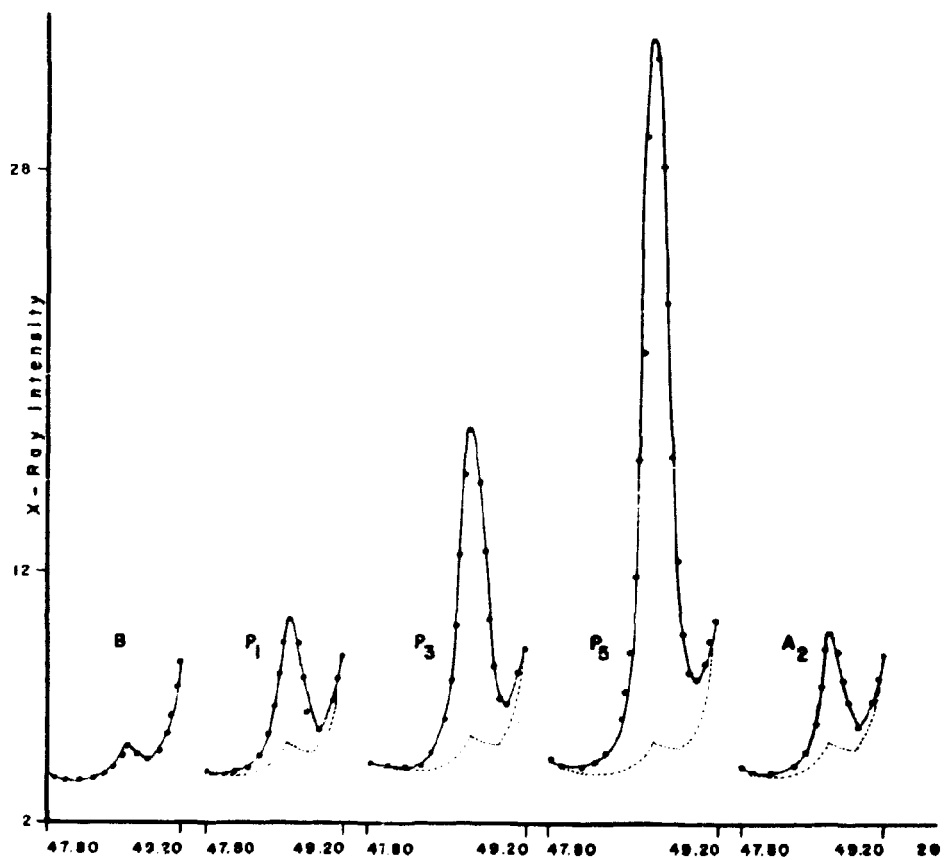


Figure 4 — Step-by-step scanning profile for Ni from blank (B), standard (P<sub>1</sub>, P<sub>3</sub> and P<sub>5</sub>) and sample (A<sub>2</sub>) pellets. Blank profiles (dashed lines) drawn under standard and sample profiles indicate almost complete elimination of matrix-effect.

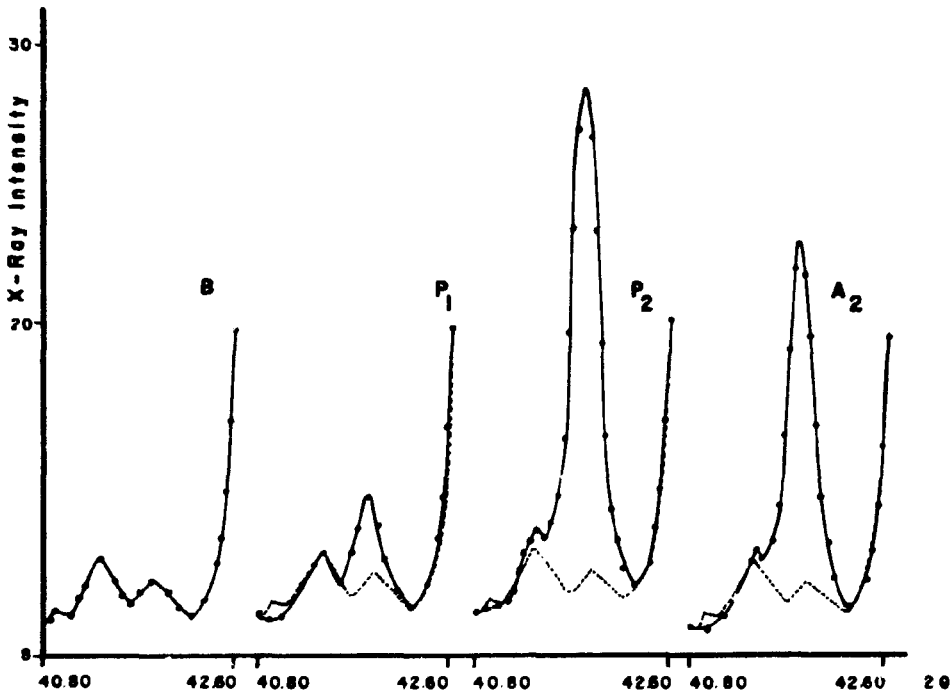


Figure 5 — Step-by-step scanning profile for Zn from blank (B), standard (P<sub>1</sub> and P<sub>2</sub>) and sample (A<sub>2</sub>) pellets. Blank profiles (dashed lines) drawn under standard and sample profiles indicate almost complete elimination of matrix-effect.

Zn : (281 ± 6) ppm

Ni : (80 ± 4) ppm

Cu : (35 ± 1) ppm

Figures 6, 7 and 8 are calibration curves for Zn, Ni and Cu plotted according to "least-squares" method

## CONCLUSIONS

A quantitative method was successfully established for the trace element analysis of Zn, Cu and Ni in the phosphorite ore from Olinda. As we wanted a method applicable to other types of ores we were compelled to adopt the mentioned technique of dilution with a melting flux.

Correction for matrix effects was accomplished by seeking the interfering elements (qualitative and quantitative determination) already existent in the ore. Their interference was caused either by absorption or by enhancement. Our search started at the International Tables' list of elements that absorb Zn, Ni and Cu radiation. All elements from that list were investigated, and Ca and Fe showed up in the phosphorite ore. Their contents were exactly determined enabling us to obtain standard pellets, which in turn allowed an almost perfect correction for matrix effects upon Zn, Ni and Cu determinations, by means of calibration curves.

On the other hand, as Ca and Fe amounts had to be known, we were obliged to develop another analytical method at the same time, destined to detect medium-to-high concentrations of said elements.

This method (double dilution) is almost unrestrictedly applicable to any major constituents of any type of ore.

Nevertheless a few remarks ought to be made when our method is to be employed in routine analysis.

If a large number of samples is to be analysed, application of the method exactly as described becomes a rather cumbersome task; it would be impractical to determine Fe and Ca contents for each sample as well as standard pellets to construct calibration curves.

In such cases a group of 5 samples may be chosen at random provided their Fe and Ca contents vary considerably from sample to sample, and their Zn, Ni and Cu contents exactly determined by the method as described before. With these data, it is mathematically possible to establish the Fe and Ca influence upon Zn, Ni and Cu measurements for the remaining samples. The mathematical correction is done extrapolating Fe and Ca influences (that depend on the amount of Fe and Ca present) to 0% Fe and Ca concentrations.

Once this procedure is followed, there is still a need to determine Fe and Ca contents for each remaining sample. It can be done easily by calibrating the data directly from the Fe and Ca contents in the 5 samples and determining Fe and Ca amounts in the remaining samples by direct comparison.

A quite similar procedure was successfully tested by our group when investigating Zn contents in samples collected during an ore prospection expedition conducted by the C.P.R.M. (Mineral Resources Prospection Company) in the State of São Paulo<sup>(12)</sup>.

Finally, a few remarks ought to be made concerning errors involved on using our method.

An X-ray fluorescence method, like all other instrumental methods for chemical analysis is subject

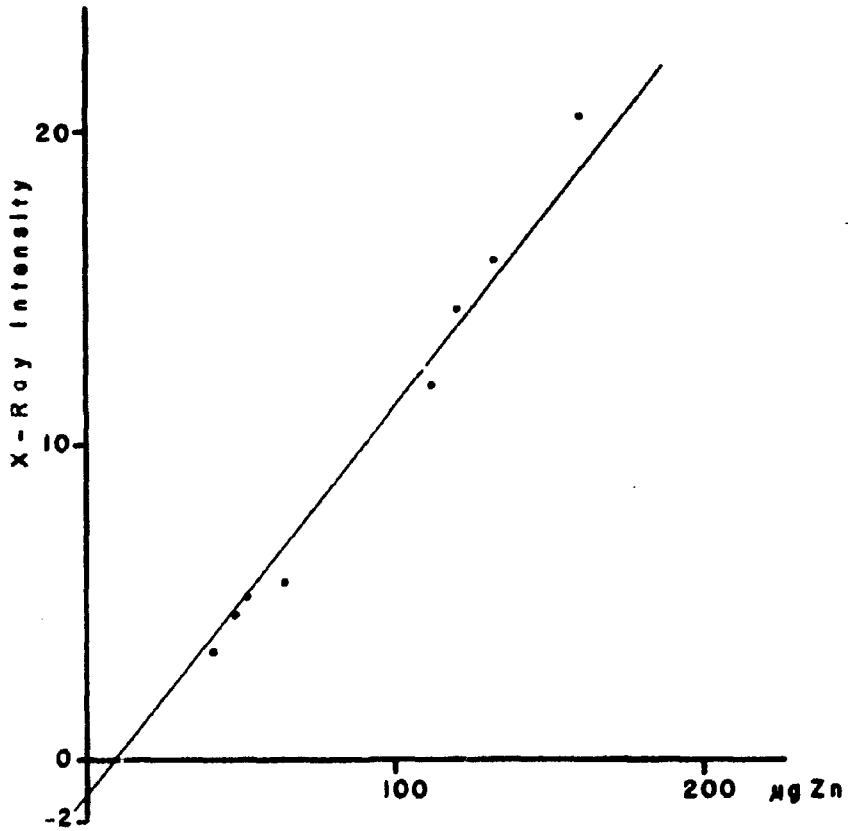


Figure 6 — Calibration curve for Zn based on data from table II.

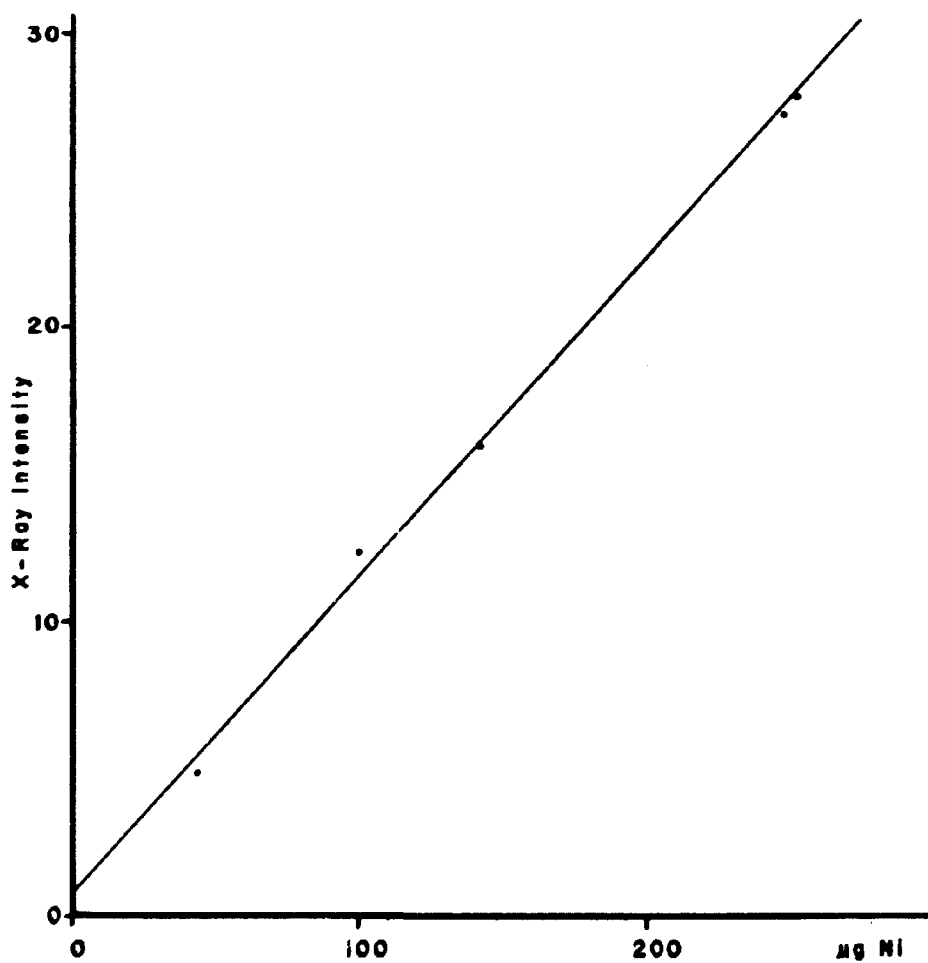


Figure 7 - Calibration curve for Ni based on data from table II



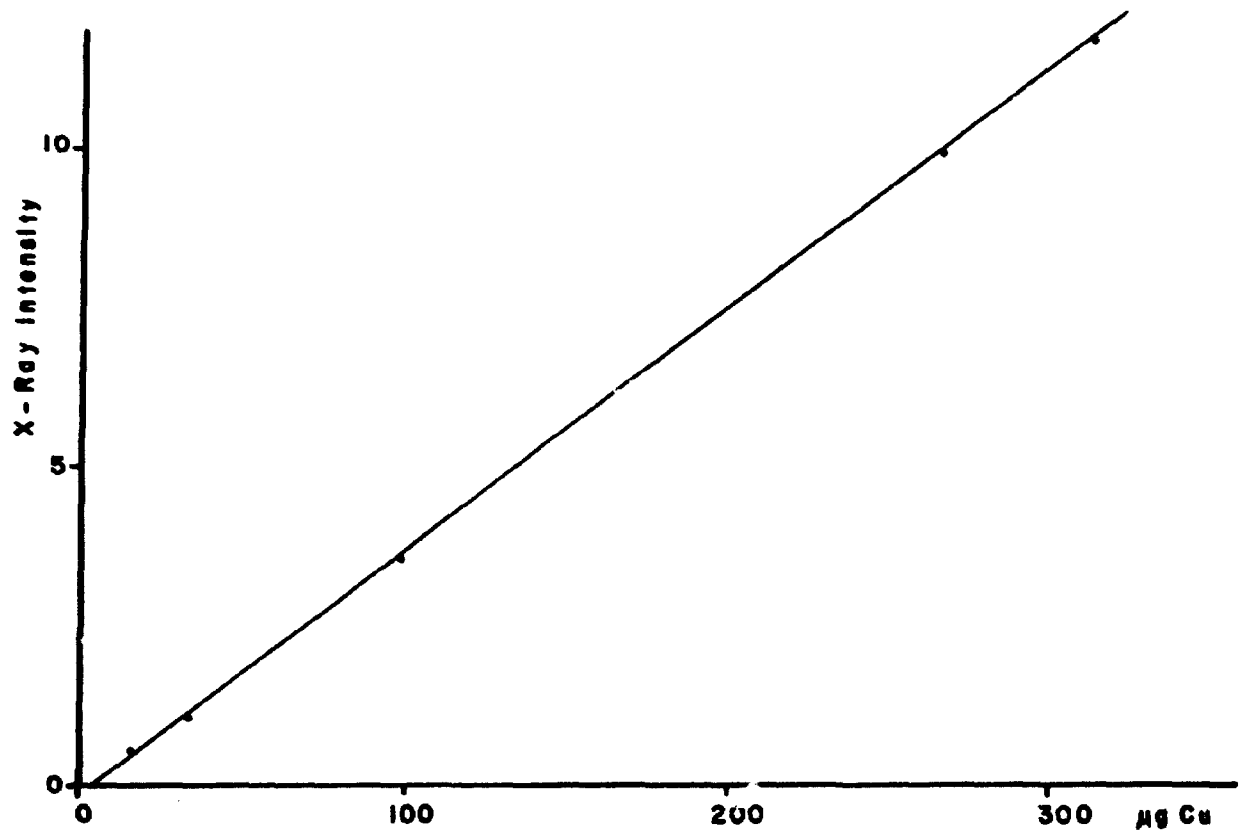


Figure 8 - Calibration curve for Cu based on data from table II.

to several sources of error. The so called "random errors" arise from X-ray intensity measurements, generator instability and type of apparatus employed. In case standards are assumed to be free from errors, the main sources of systematic errors remain the ones due to the equipment and to the samples themselves.

In as much as the accuracy of any analysis depends upon random and systematic errors — invariably associated — it is important to assess the magnitude of individual errors, thus being able to control them. It is common practice in X-ray fluorescence spectrometry to reduce random equipment errors to such an extent that the error due to counting statistics is the limiting error within the range of stability of a given combination of generator and X-ray tube<sup>(8)</sup>

Systematic equipment errors were rather satisfactorily controlled because a highly stabilized (.003%) generator is available at our laboratories, thus allowing great reproducibility of the tube voltage<sup>(13)</sup>. Consequently, residual systematic errors due to the sample remained as the only significant ones. Correction for them — referred to as "matrix effects"<sup>(\*)</sup> — deserved considerable efforts and it is certainly one of the crucial parts of our work.

Hence, as one of the main sources of error was detected and controlled, our analysis reached an accuracy as high as  $\pm 1$  ppm for Cu,  $\pm 4$  ppm for Ni and  $\pm 6$  ppm for Zn.

These errors were estimated for the case of most unfavorable conditions. These values represent therefore, the worst error estimate. In practice, figures could be much lower.

## APPENDIX

### An Elemental Determination of Fe and Cu using the Double Dilution Method.

#### INTRODUCTION

The double dilution method was developed by Tertian<sup>(15,16)</sup> and is applicable to X-ray fluorescence analysis in solutions, especially in solid solutions such as obtained by fusion methods. Tertian demonstrated that the fluorescent intensity  $Y$  of a given element and the concentration  $x$  of the sample in the flux or solvent are connected by the rather simple expression:

$$Y = \frac{1}{1 + \varphi x} \quad (1)$$

Where  $\varphi$  is a matrix factor, characteristic of the sample to be analysed dissolved in a given flux, for the fluorescent element. Therefore if two measurements of  $Y$  at two different concentrations  $x$  are performed,  $\varphi$  is readily calculated, which permits correction of the obtained intensities for the so called matrix effects, namely absorption and enhancement effects.

Thus, we attempted to establish and confirm the advantages of employing such method, as stated by Tertian:

- application possible to any fluorescent element at any concentration or material, without assumption about the nature or composition of the sample when unknown
- no systematic calibration required, but only a few fixed standards instead at the limit, and a

(\*) Besides interelemental interaction (absorption and enhancement), other physical parameters are considered as matrix effects, too. These are mainly particle size and surface roughness. However, the latter was duly diminished by an homogeneous melted pellet preparation.

single one for each element consisting of a pure compound or of an accurately known sample

## FUNDAMENTALS

Dissolving the unknown sample at two different concentrations (for instance  $x$  and  $2x$  in the flux), the net measured intensities of a given element should be given by (1):

$$Y_1 = \frac{x}{1 + \varphi x} \quad (2)$$

$$Y_2 = \frac{2x}{1 + 2\varphi x} \quad (3)$$

The change in the  $Y$  intensity as a function of the concentration  $x$  will not be linear; our purpose is to transform the non linear  $Y$  curve into a linear  $Y'$  curve making use of equation (1) (figure A)

In order to obtain the linear  $Y'$  curve,  $\varphi$  must be previously determined.

### a) Determination of $\varphi$

The relation  $r$  between  $Y_1$  and  $Y_2$  is obtained from (2) and (3)

$$r = \frac{Y_2}{Y_1} = \frac{2(1 + \varphi x)}{1 + 2\varphi x} \quad (4)$$

Therefore, 
$$\varphi = \frac{(2 - r)}{2x(r - 1)}$$

or 
$$\varphi = \frac{1}{2x} \cdot \frac{2 - (Y_2/Y_1)}{(Y_2/Y_1) - 1} \quad (5)$$

Analysis of equation (5) shows that intensity measurements of two standard samples of known concentrations  $x$  and  $2x$  would suffice to determine  $\varphi$ .

### b) Construction of the linear $Y'$ curve

The linear  $Y'$  curve is constructed by converting each value of  $Y$  into the correct  $Y'$  value. Considering, for example, points  $Y_2$  and  $Y_2'$  in figure A, we have:

$$Y_2 = \frac{2x}{1 + 2\varphi x}$$

$$Y_2' = 2x$$

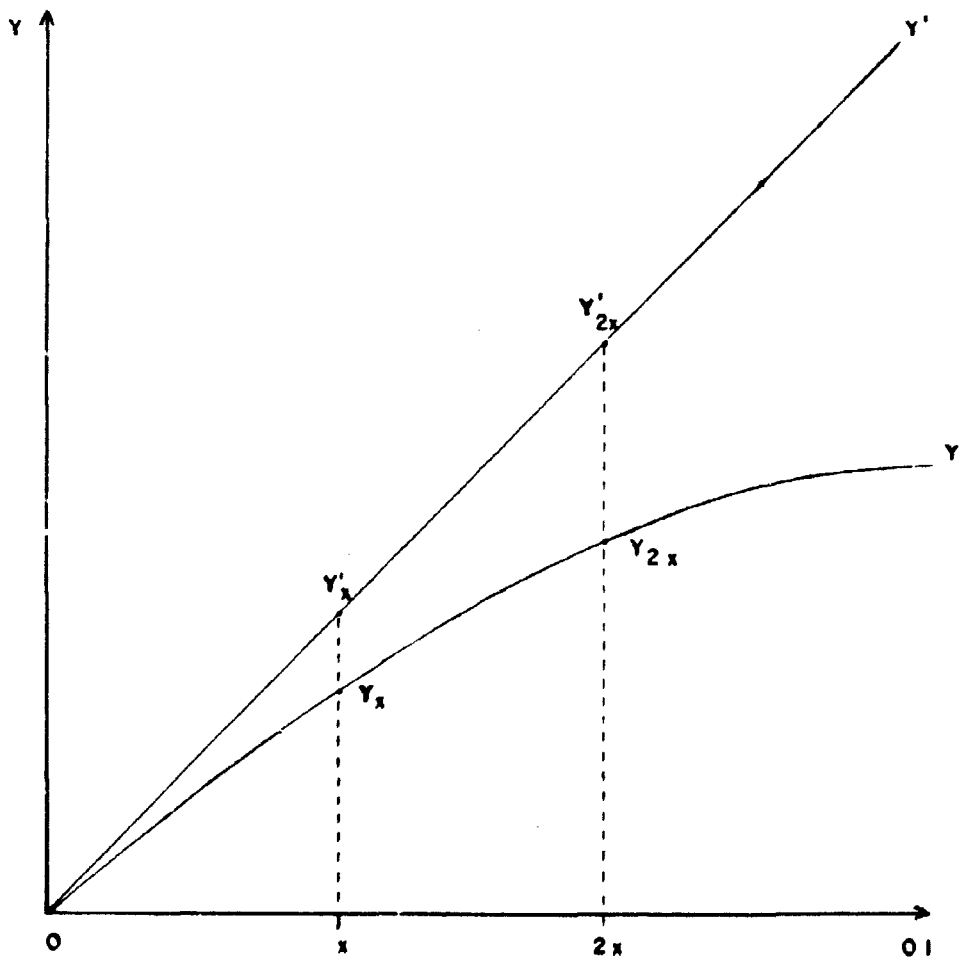


Figure A - Plot of  $f(x) = \frac{x}{1+\varphi x}$  between  $x=0$  and  $x=1$  (for  $\varphi=10$ )  $Y'$  is the corrected function

The relation  $q$  between them is immediate:

$$q = \frac{Y'_2}{Y_2} = 1 + 2\phi x$$

Inserting equation (4) into the above equation,

$$q = \frac{1}{r - 1} \quad (6)$$

Therefore, each experimental intensity  $Y_i$  may be converted into a corrected  $Y'_i$  value employing the calculated  $q$  factor, thus transforming a non-linear calibration curve  $Y$  into a linear curve  $Y'$ , effectively used when ever analysis is being conducted, as follows:

Let  $Y_x$  and  $Y_{2x}$  be the experimental intensities of the samples with concentrations  $x$  and  $2x$ , i.e. 1 : 2 ratio. We have:

$$\frac{Y'_{2x}}{Y_{2x}} = q$$

or 
$$Y'_{2x} = \frac{Y_{2x}}{r - 1}$$

but, 
$$r = \frac{Y_2}{Y_1} \quad \text{by equation (4) and then,}$$

$$Y'_{2x} = \frac{Y_{2x}}{(Y_{2x}/Y_{1x}) - 1} \quad (7)$$

The corrected value  $Y'_{2x}$  is proportional to  $2x \cdot C$  where  $C$  is the concentration of the desired component.

Any ratio may be chosen for the concentration  $x$  instead of the 1 : 2 value, used in the above example, and equally simple equations are thus obtained for ratios such as 1 : 3, 1 : 4 etc.

$$Y'_{3x} = \frac{2Y_{3x}}{(Y_{3x}/Y_x) - 1} \quad (8)$$

$$Y'_{4x} = \frac{3Y_{4x}}{(Y_{4x}/Y_x) - 1} \quad (9)$$

Analysis of equation (5) shows that intensity measurements for only two standard-samples with their concentrations  $x$  and  $2x$  previously known would suffice to determine  $\phi$ ; desired concentration  $C$  is obtained recalling  $Y'_{2x}$  is proportional to  $2x \cdot C$ . The proportionality factor is obtained with the aid of standards

## EXPERIMENTAL PROCEDURE

Although only two dilutions are enough to perform the analysis (double dilution), it is customary to repeat it using several proportions such as 1 : 2 : 4 : 6 etc. to assure complete validity of equation (1), and simultaneously determine the dilution range for which Tertian's relation holds.

This way, the sample pellets were prepared by adding proportional quantities of the phosphorite ore to 3 grams of borax, according to Table III, which also shows data concerning preparation of the Ca and Fe standard pellets (at the same proportion of the sample pellets) with 3 g of borax.

Table III  
Quantities involved in standard pellets (P<sub>i</sub>), sample pellets (A<sub>i</sub>)  
and blank pellet (B) preparations

Pellets	Borax	phosphorite (mg)	Ca (mg)	Fe (mg)
B	3 000	—	—	—
P <sub>1</sub>	3 000	—	5	2
P <sub>2</sub>	3 000	—	10	4
P <sub>3</sub>	3 000	—	20	8
P <sub>4</sub>	3 000	—	40	16
P <sub>5</sub>	3 000	—	60	20
A <sub>1</sub>	3 000	25	—	—
A <sub>2</sub>	3 000	50	—	—
A <sub>3</sub>	3 000	100	—	—
A <sub>4</sub>	3 000	200	—	—
A <sub>5</sub>	3 000	300	—	—
A <sub>6</sub>	3 000	400	—	—

Initially, profiles of the FeK $\alpha$  and CaK $\alpha$  peaks were obtained to be compared to standard, sample and blank — pellets. In figure B FeK $\alpha$  profiles for the 3 samples can be seen; background is practically zero and it is evident that the blank sample presents a very small Fe contamination, due either to the Z ray tube target or the flux (borax) used.

Figure C shows Ca background is also zero, whereas the blank pellet is not contaminated by calcium.

As both backgrounds are identical we may confidently admit the same "matrix factor" upon both standard and sample pellets.

Table IV presents a summary of the experimental conditions employed in our work.

Table IV  
Experimental Parameters Utilized to Measure CaK $\alpha$  and FeK $\alpha$   
lines. All measurements performed in vacuum

Element	Calcium	Iron
Tube voltage (hV)	35	35
Tube current (mA)	20	20
Crystal analyser	EDDT	LiF(200)
Target	W	W
Angular Position ( $2\theta$ )	44 85°	57 54°
Base Line (V)	3.4	2.9
Channel Width (W)	3.0	4.8
Counter	Proportional	Scintillation

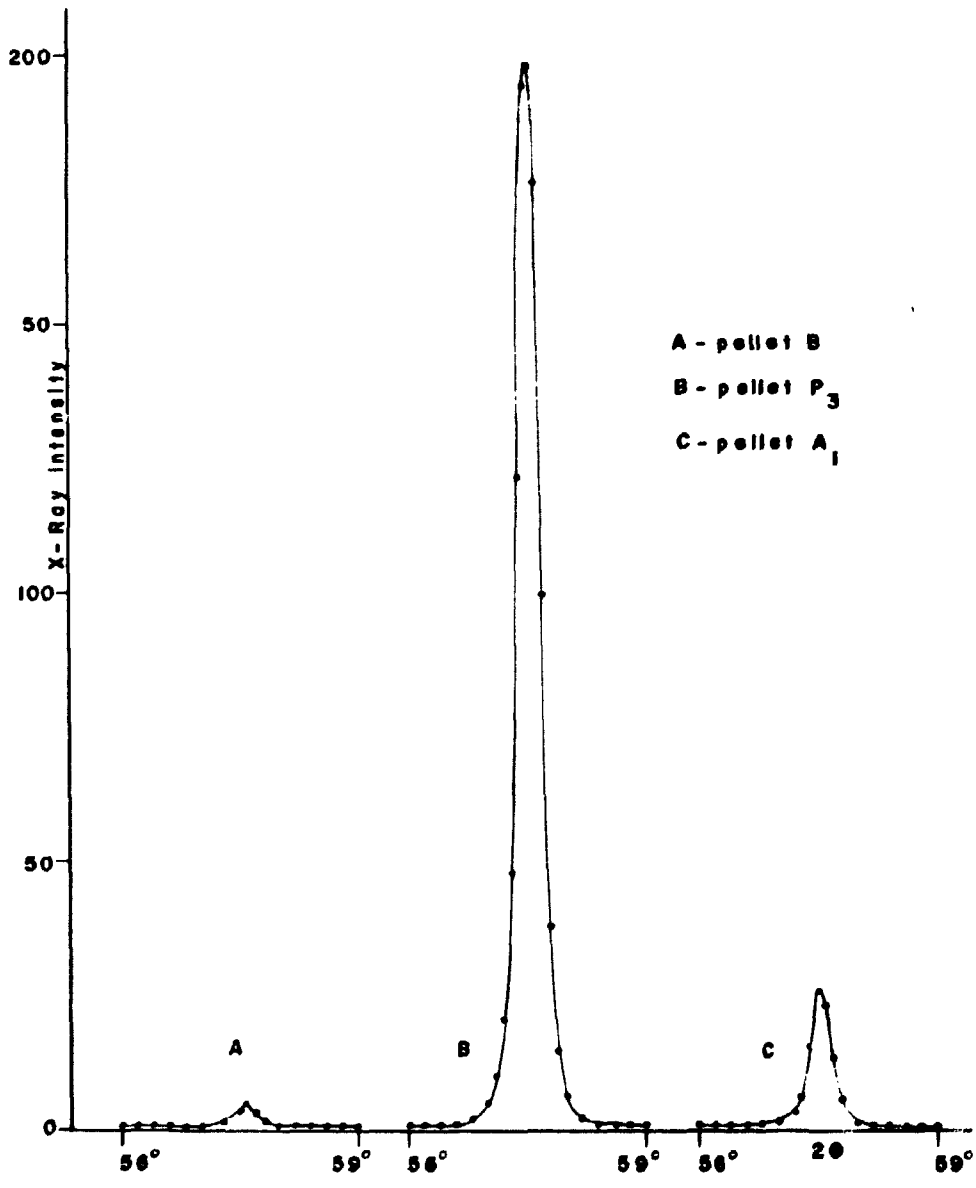


Figure B - Fe K $\alpha$  peak profiles for blank, standard and sample pellets

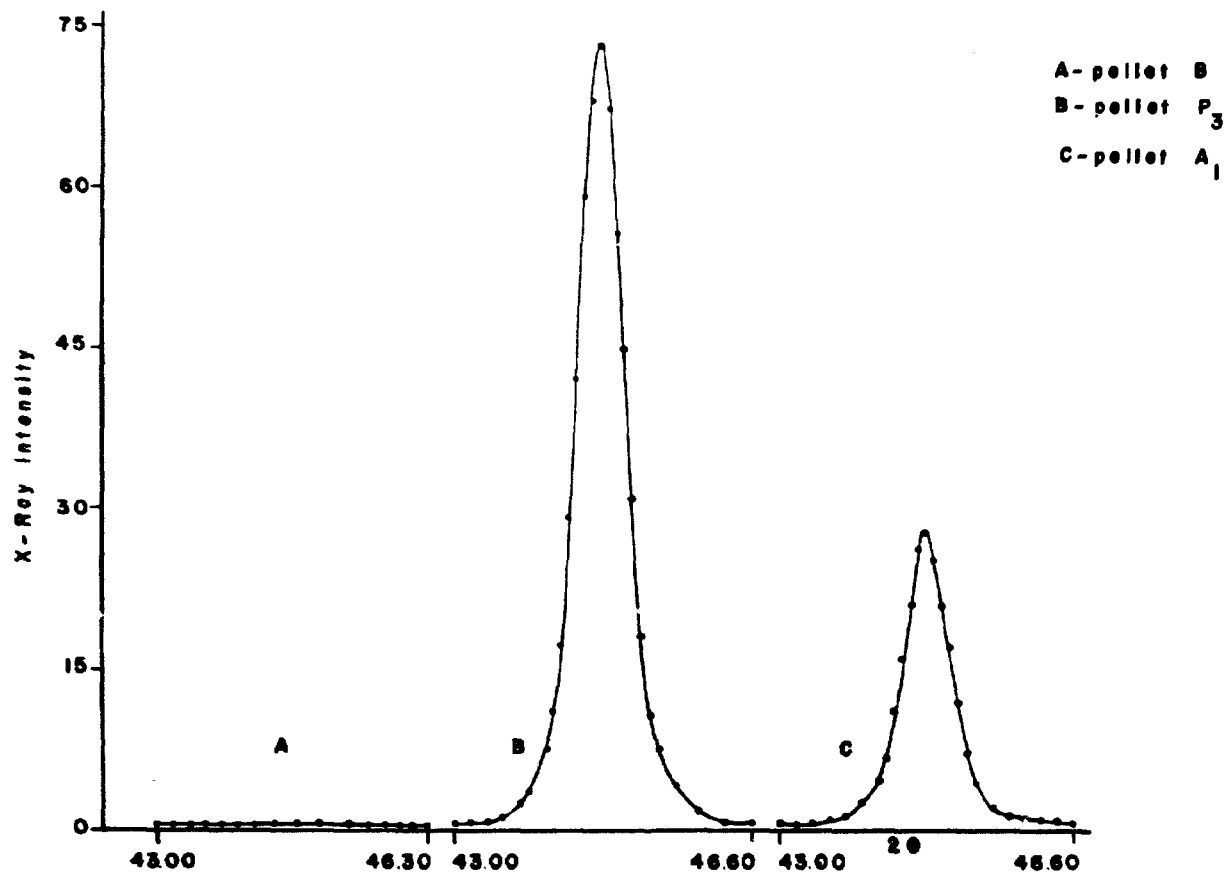


Figure C - Ca  $K_{\alpha}$  peak profiles for blank, standard and sample-pellets.



With the experimental intensities  $Y$ , corresponding to  $\text{CaK}\alpha$  and  $\text{FeK}\alpha$  lines for all samples listed in table I, we are able now to compute the corrected intensities  $Y'_i$ , using expressions (7), (8) and (9) as presented in table V (for Ca) and table VI (for Fe) as follows:

Table V  
Measured and corrected intensities for  $\text{CaK}\alpha$  line.

Pellets	ore content (mg)	$\text{CaK}\alpha$ intensities ( $Y_i$ )	Corrected Intensities ( $Y'_i$ )
$A_1$	25	12 024	—
$A_2$	50	22 077	26 407
$A_3$	100	41 868	50 606
$A_4$	200	70 004	101 337
$A_5$	300	85 694	153 872
$A_6$	400	98 456	205 459
Calcium content (mg)			
$P_1$	5	9 187	—
$P_2$	10	17 187	19 676
$P_3$	20	34 636	37 511
$P_4$	40	65 187	74 866
$P_5$	60	82 674	113 690

Linear and non-linear calibration curves for  $\text{CaK}\alpha$  and  $\text{FeK}\alpha$  intensities as functions of mg phosphorite, mg Ca (for  $\text{CaK}\alpha$ ) and mg Fe (for  $\text{FeK}\alpha$ ) were constructed and are given in figures D, E, F and G based on data from tables V and VI

The absolute linearity obtained for the corrected intensity calibration curve attests complete validity of Ternan's relation in the case of phosphorite, for which the amounts of Fe and Ca were determined as

$$\text{Ca } (27.2 \pm 3)\%$$

$$\text{Fe } (3.3 \pm 1)\%$$

The data above are in quite good agreement with the ones obtained by semi-quantitative optical spectrography methods by Marivone G de Almeida<sup>(2)</sup> using the same sample, that yielded the following values

$$\text{Ca } 25\%$$

$$\text{Fe } 5\%$$

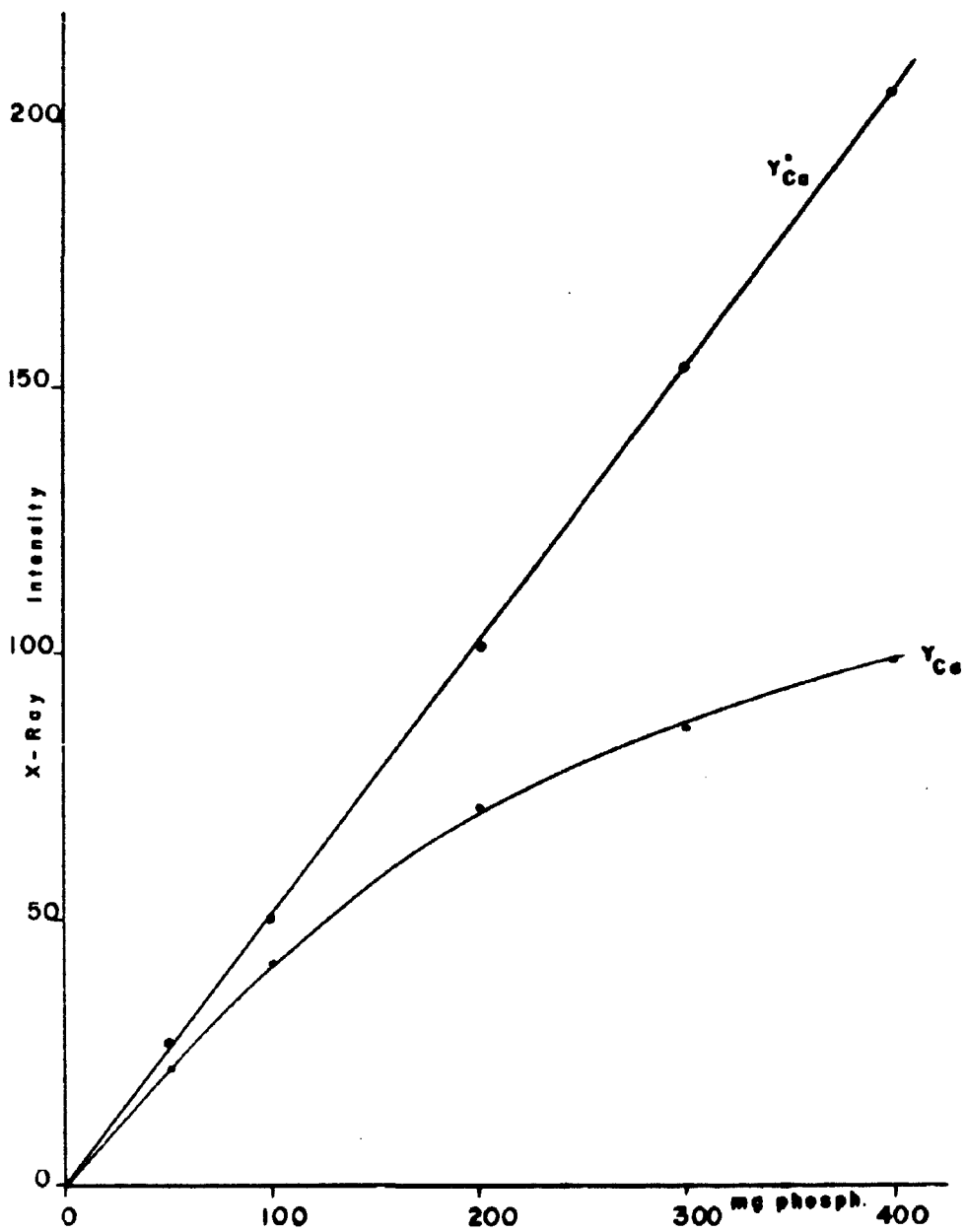


Figure D - Measured Ca K $\alpha$  intensities vs. mg phosphorite (non-linear  $Y_{Ca}$  curve) and corrected intensities vs mg phosphorite (linear  $Y'_{Ca}$  curve)

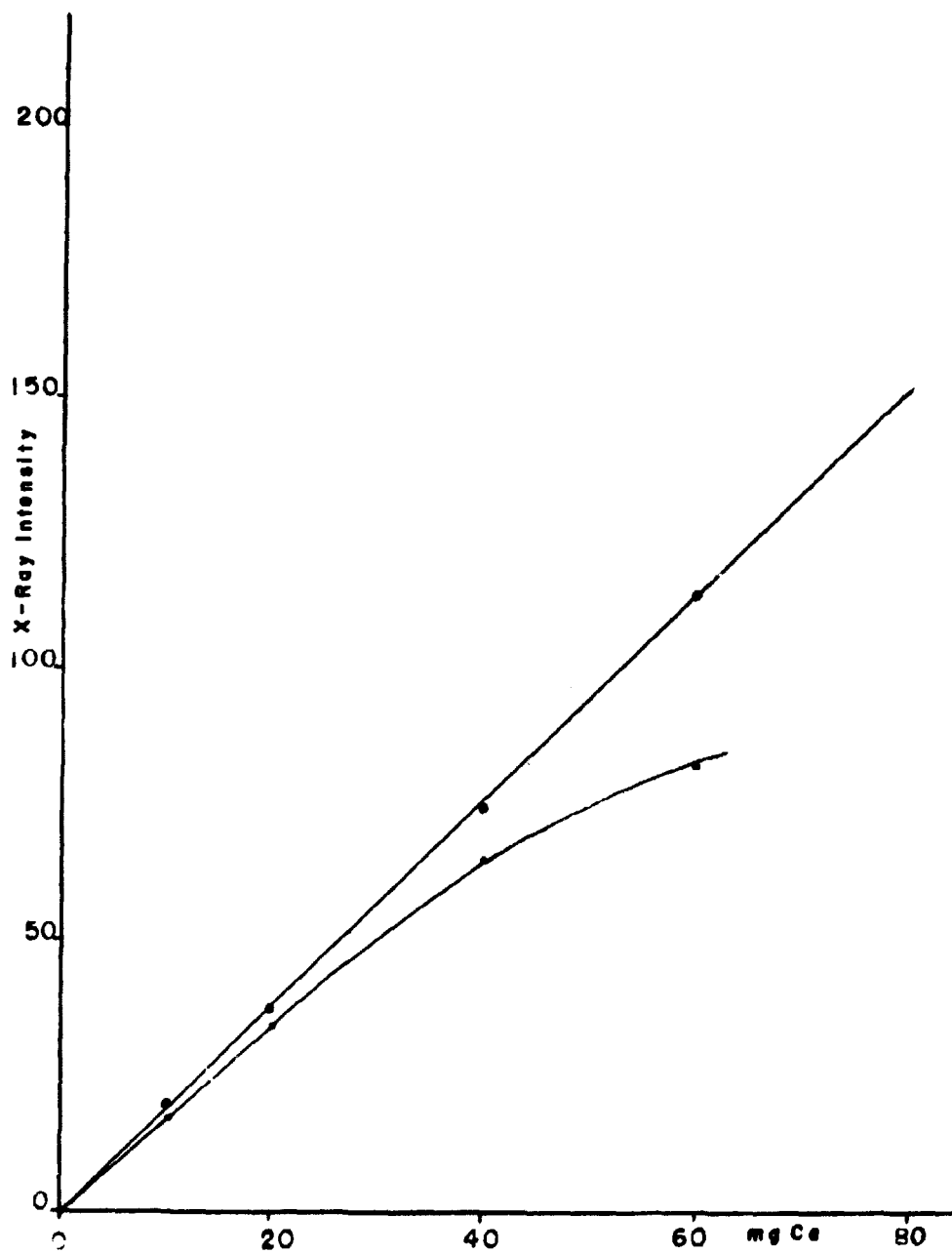


Figure E - Measured Ca K $\alpha$  line intensities vs mg Ca (non-linear Y<sub>Ca</sub> curve) and corrected intensities vs mg Ca (linear Y'<sub>Ca</sub> curve).

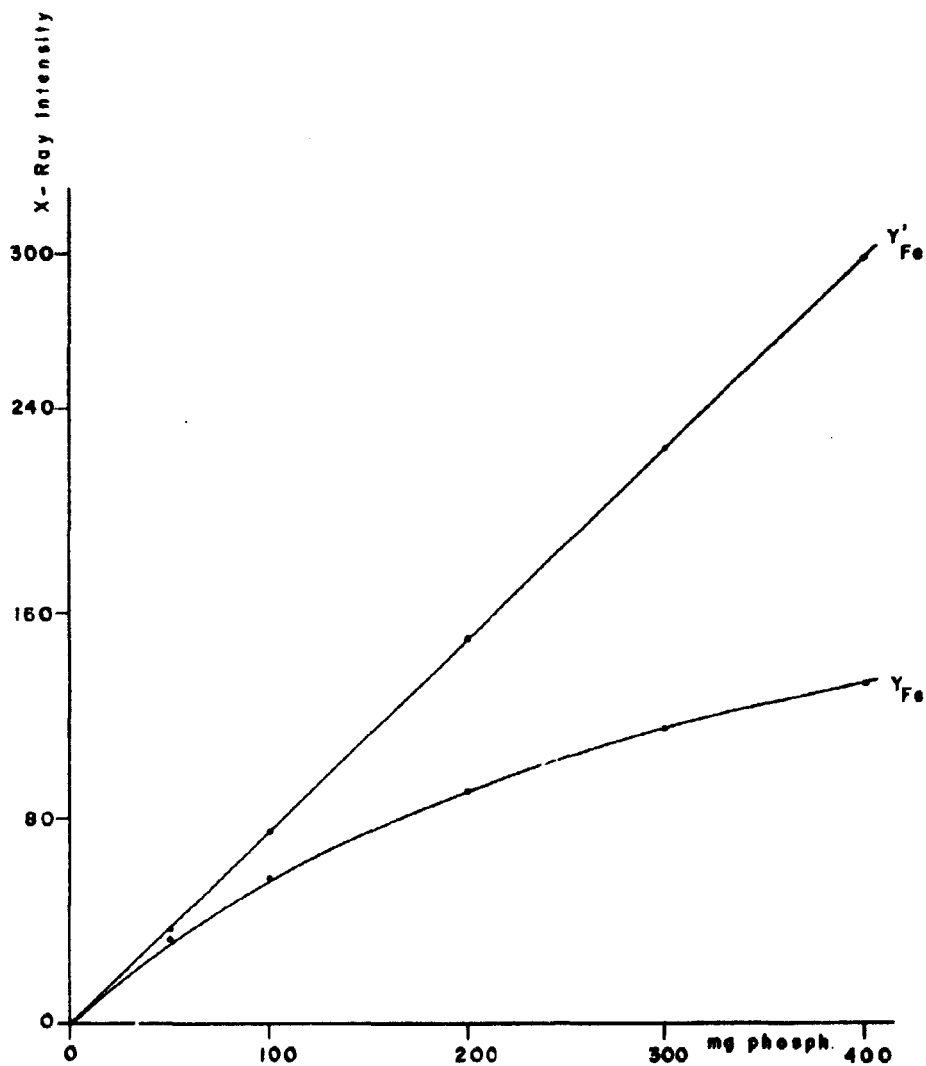


Figure F - Measured Fe K $\alpha$  intensities vs. mg phosphorite (non-linear  $Y_{Fe}$  curve) and corrected intensities vs. mg phosphorite (linear  $Y'_{Fe}$  curve)

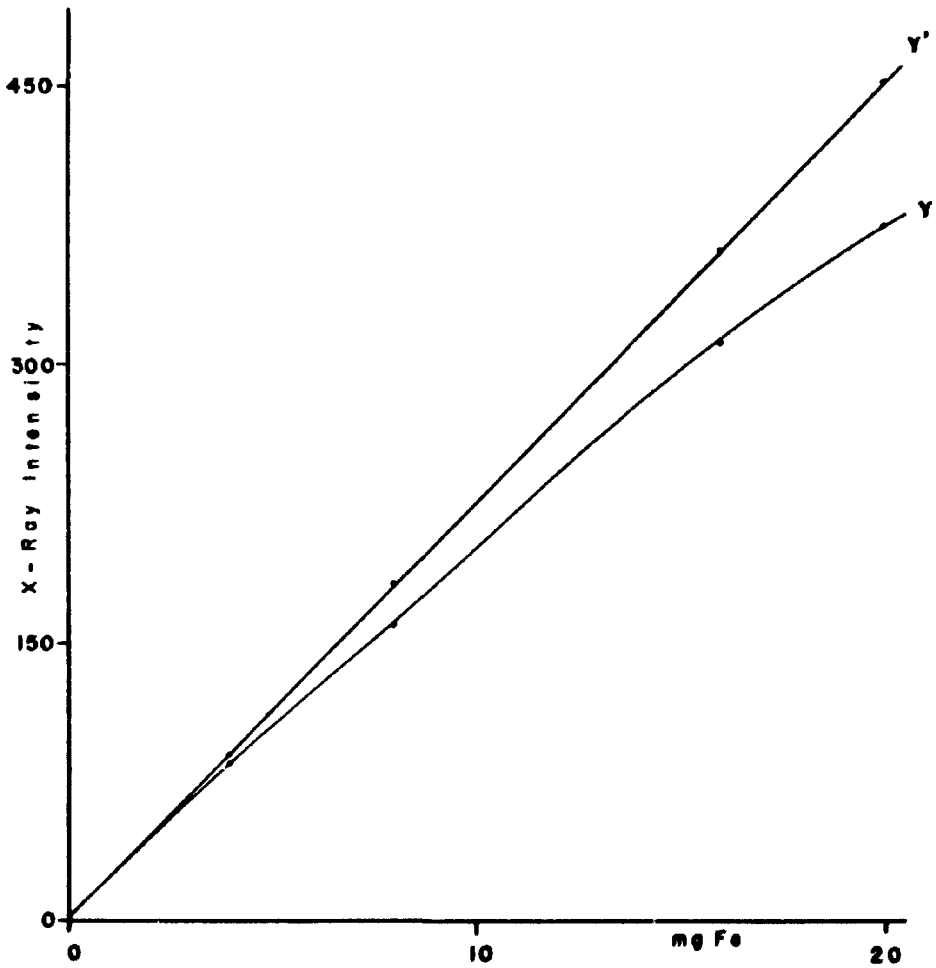


Figure G - Measured Fe  $K\alpha$  line intensities vs. mg Fe (non-linear Y Fe curve) and corrected intensities vs mg Fe (linear  $Y'_{Fe}$  curve).

## RESUMO

Estabeleceu-se um método analítico quantitativo utilizando técnicas de fluorescência de raios X para a determinação de traços de Zn, Cu e Ni em fosforita de Olinda, PE.

Diversas razões indicaram nos a escolha do método de dupla diluição usando borax como fundente.

Estudos preliminares indicaram que minérios diluídos em borax na forma de amostras fundidas apresentavam considerável efeito matriz com relação ao elemento a ser analisado.

Posteriormente foi possível identificar elementos presentes no minério, e que interferiam na determinação de Zn, Cu e Ni. Tais elementos eram Cu e Fe e seus teores foram determinados.

A adição de quantidades apropriadas de Fe e Ca aos padrões permitiu nos minimizar os efeitos de matriz sem a indesejável introdução de elementos não pertencentes originalmente ao minério. Além disso, a necessidade de se conhecer as quantidades exatas de Fe e Cu presentes no minério nos levaram ao desenvolvimento simultâneo de outro método analítico específico para elementos em média e alta concentrações. Neste método também é utilizada a técnica de diluição por fusão.

Ambos os métodos apresentam diversas vantagens se comparados aos usuais, sendo as seguintes dignas de menção:

- análise quantitativa com grande reprodutibilidade de resultados
- é aplicável, em princípio, a todos os tipos de minérios assim como a outros materiais.
- as fontes de erros predominantes podem ser controladas, permitindo alcançar precisões tais como  $\pm 1$  ppm para Cu,  $\pm 1$  ppm para Ni,  $\pm 6$  ppm para Zn e  $\pm 0,1\%$  para Fe e Ca, sob as condições mais desfavoráveis.

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#### ACKNOWLEDGEMENTS

We wish to thank Mr Jose Roberto S Vasconcellos for his help gathering most experimental data and drawing our figures

We acknowledge also Ms Marilza Redigolo who carefully typed our manuscripts

