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STUDY OF THE EFFECT OF SOME OF THE EXPERIMENTAL PARAMETERS
ON THE X-RAY FLUORESCENCE DETERMINATION OF TRACES OF HAFNIA
IN HIGH PURITY ZIRCONIA

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Jura Mohammad Qurbani, P. P. Khanna and R. M. Agrawal
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INIS Subject Category : B11

Descriptors

ZIRCONIUM OXIDES

IMPURITIES

HAFNIUM OXIDES

X-RAY FLUORESCENCE ANALYSIS

QUANTITATIVE CHEMICAL ANALYSIS

X-RAY SPECTROMETERS

TRACE AMOUNTS

COLLIMATORS

SCINTILLATION COUNTERS

PROPORTIONAL COUNTERS

X-RAY TUBES

ABSTRACT

The effect of the following parameters,

- (i) Analytical lines $\text{HfL } \alpha_1$ or $\text{HfL } \beta_{1,6}$ or $\text{HfL } \beta_2$
 - (ii) Detectors - scintillation or gas flow proportional
 - (iii) Collimators - fine or coarse
 - (iv) X-ray tube voltage, current and power
 - (v) Order of diffraction: I or II of analysing crystal LiF (200),
- on the precision of the results and the sensitivity of the method in the x-ray fluorescence determination of traces of hafnia in high purity zirconia, has been studied.

Philips semiautomatic x-ray spectrometer PW 1220 with associated equipment has been used. Synthetic standards containing HfO_2 in the range 20 ppm to 1% in ZrO_2 , presented as double layer pellets have been used. LiF (200) analysing crystal, tungsten target x-ray tube, automatic pulse height selection and pulse height discrimination were used in all the cases. The set - "HfL $\beta_{1,6}$ analytical line, fine collimator and gas flow proportional counter detector" - gave the best performance.

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1. INTRODUCTION

Zirconium is used extensively for cladding enriched fuel rods in nuclear power plants because of its low thermal-neutron capture cross-section and its resistance to corrosion by super heated steam. Hafnium, however, has a much larger neutron capture cross-section and its presence in zirconium is undesirable. Separation of traces of hafnium from zirconium is an extremely difficult process because the two elements have almost identical chemical properties owing to their similar ionic radii ($\text{Hf}^{4+} = 0.78 \text{ \AA}$ and $\text{Zr}^{4+} = 0.79 \text{ \AA}$) and outer electronic structures. Determination of traces of Hf in Zr by chemical methods is not possible because of the same reasons. Methods involving prior separation and subsequent determination are time-consuming. In order to determine traces of hafnia in zirconia (which is a product for obtaining the metal subsequently), one has to resort to the instrumental methods of analysis.

Mass spectrometry gives high sensitivity but requires elaborate equipment. Neutron activation also gives high sensitivity but requires facility of a nuclear reactor or neutron source. Optical emission spectrography gives reasonable sensitivity but requires special precautions and procedures to attain it. X-ray fluorescence spectrometry is rapid,

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convenient and gives adequate sensitivity. However, several experimental parameters have to be optimized initially, to attain the required sensitivity with adequate precision.

K-lines of Hf cannot be used for the analysis, because of the high excitation potential for the lines of the K-series of Hf, non-availability of suitable analysing crystals for this spectral region and the high background due to scattering. Therefore, one has to use the lines of the L-series. However, the L_{α_1} line of Hf, the strongest in the L-series has an almost complete overlap due to the second order K_{α_1} line of Zr, which being from the matrix appears quite strong even in the second order reflection. Even after pulse height discrimination, residual intensity of ZrK_{α_1} will be much higher compared to the L_{α_1} line from Hf, the trace element. Similarly, $L_{\beta_{1,6}}$ line of Hf, the second strong line of the L-series has an appreciable overlap from the second order ZrK_{β_2} line. Use of still weaker L_{β_2} line of Hf, though free from interference, results in lowering the precision and the sensitivity. Brookes and Townshend¹ in their review article have discussed the methods used by different workers to overcome or reduce the interference problem in order to attain adequate sensitivity and precision, which to a considerable extent depend upon the equipment available and the experimental parameters selected. A systematic study of the various available experimental parameters and their effect on the sensitivity and precision in the determination of traces of Hf in Zr is therefore highly desirable in order to select the optimum conditions for attaining the adequate precision and sensitivity. The work described in the following paragraphs

has been undertaken with the above considerations.

2. EQUIPMENT

Philips semiautomatic x-ray spectrometer PW 1220, with the associated ultrastabilised 100 kV x-ray generator PW 1140 and the measuring electronic panel PW 1360 and other accessories have been used. The spectrometer provides choice of three analysing crystals, collimators (fine or coarse), detectors (scintillation or gas-flow proportional), air or vacuum paths and facilities for loading four samples which can be stationary or spinning in the measuring position. It also provides facilities of the crystal attenuator resistor unit and a sine Θ potentiometer for automatic pulse height selection. Amplifier/analyser of the electronic panel PW 1360, is used for pulse height discrimination. Facilities for print out of the data are also available.

The x-ray spectrometry tube of maximum rating 2.7 kW is powered from the ultrastabilised x-ray generator PW 1140 in which the high tension and the tube current are both stabilised to within .01%. The generator can provide high tension upto 100 kV.

P-10 gas (90% Argon: 10% Methane mixture) is used in the flow proportional counter. The gas flow system has been provided with the gas density compensator to compensate the effect of the changes of the atmospheric pressure and temperature on the density of the flowing gas which affects the pulse heights of the signals from the detector. The two counters - scintillation and the gas flow proportional - are mounted in tandem so that the beam diffracted by the analysing crystal can be intercepted by both the detectors.

3. SAMPLE PRESENTATION

In order to make use of a small quantity of the sample for presenting to the spectrometer in a reproducible way, the technique of double layer pellet has been used. 500 mg of the sample or standard is accurately weighed and thoroughly mixed with an equal proportion of boric acid (as a binding material) in an agate mortar. Initially a pellet of pure boric acid is made in the die at a compression force of 2 tons. Then the plunger is removed and the sample - boric acid mixture is spread over the pellet in the die as uniformly as possible, the plunger is replaced again and the sample layer made further uniform by gently pressing and rotating the plunger. Later on, the final compression is carried out at a total force of 20 tons to get a double layer pellet. The base pellet provides the necessary strength to the thin second layer of the sample. This method of presentation of the sample in the x-ray beam is having several advantages - a small quantity of the sample is required, the compactness is reproducible, sample handling is easy, the standards/samples can be preserved for future use or reference etc. The pellets are $1\frac{1}{4}$ " in diameter and are of the correct size for loading in the special sample holder of the spectrometer. The pellets are loaded with the thin sample layer downwards in the sample holder, so that the sample surface is directly exposed to the x-ray beam during the measurements.

Initially, by preliminary experiments the critical amount of the sample, suitable proportion of the binding material, and optimum force of compression were determined. The amount of the sample should be sufficient, so as to give a layer of thickness greater than the critical

thickness for the analytical wavelengths used and the compression force should be sufficient to eliminate the particle size effects, if any.

4. STANDARDS

Synthetic standards are prepared by dry-mixing the calculated amounts of *spec-pure* hafnium oxide with zirconium oxide in an agate mortar. The grinding and mixing is carried out for a sufficient length of time to ensure homogeneity. Initially, a master standard containing 10% HfO_2 in ZrO_2 has been prepared, which has been subsequently diluted with pure ZrO_2 to give the standards in the range 20 ppm to 1%. The oxides supplied by Johnson Matthey were used and were ignited and subsequently cooled in a desiccator before weighing the requisite amounts. These standards were converted into double layer pellets by the procedure already described under 'Sample Presentation'.

5. BACKGROUND CORRECTIONS

A 'blank' standard prepared in the manner similar to the other standards but without the deliberate addition of the impurity element has been used for the background measurements. This method of background correction is particularly useful for trace level regions particularly when due to interference or insufficient resolution, one has to measure the fluorescence intensity of a trace element against a high background due to the intense radiation from the matrix element. This method of background correction is having the advantage that the contribution to the fluorescence intensity due to the presence of residual amount of impurity element, in the materials used for the preparation of the standards,

is taken care of.

6. EXPERIMENTAL CONDITIONS AND OBSERVATIONS

Effect of the following parameters has been studied using LiF (200) analysing crystal and the pulse height discrimination in all the cases.

- (i) Use of $L\alpha_1$, $L\beta_{1,5}$ and $L\beta_2$ lines of Hf as analytical lines.
- (ii) Flow proportional and scintillation counters (the latter with an additional auxiliary collimator).
- (iii) Fine and coarse collimators
- (iv) High tension and the power of the x-ray spectrometry tube.
- (v) LiF (200) crystal in the first and second orders.

Suitable combinations of these parameters have been used. Various sets of parameters used in the study and the results obtained are summarised in Table I (Sets A to H).

7. RESULTS AND DISCUSSION

As mentioned in the introductory part of this report, the main difficulty in the XRF analysis of traces of HfO_2 in ZrO_2 is due to the interference of the second order Zr K-spectrum with the first order Hf L-spectrum. This is shown in Fig.1 which is a strip chart recording of the hafnium L-spectrum and the superposed K-spectrum of zirconium in the second order after pulse height discrimination, using LiF (200) analysing crystal and the scintillation counter provided with an additional auxiliary collimator (10 cm length) for higher resolution. It is clearly seen that even with the high resolution available, as is obvious from

the resolution of $ZrK\alpha_1$ and $ZrK\alpha_2$, there is an almost complete overlap of $ZrK\alpha_1$ (II) with the $HfL\alpha_1$ (I) and $ZrK\beta_2$ (II) with $HfL\beta_{1,6}$ (I). One also observes that the pulse height discrimination electronically, does not completely eliminate the II order ZrK-spectrum and that the residual intensity of second order ZrK-spectrum is appreciable even after pulse height discrimination, zirconium being the main/matrix element. It can also be observed that $HfL\beta_2$ is free from interference from second order zirconium K-spectrum. The results obtained with suitable combinations of the experimental parameters are summarised in Table I. The table gives the average count rates (counts/sec) for the peak intensity with a standard of 500 ppm nominal concentration, the background intensity (obtained from the 'blank'), and the net fluorescence intensities of the various Hf analytical lines investigated (for 500 ppm standard) in combination with other parameters. The same table also gives the standard counting errors in those measurements calculated for the given counting time and the set of 'n' observations. It also gives the calculated signal to background ratios obtained from 500 ppm standard, sensitivity, i.e., slope of the calibration curve obtained from the measurements on the complete set of standards $\left[\frac{\Delta I}{\Delta Conc} \right]$ i.e. change in count rates per unit (100 ppm) change in the concentration of HfO_2 in ZrO_2 and also the calculated detection limits for 100 seconds counting time $\left[\right]$ defined as the concentration at which the signal becomes three times the standard deviation of the background $\left[\right]$.

7.1 Sets A and B of Table I : The $HfL\alpha_1$ line being the strongest is expected to be the best choice. However, as mentioned earlier, the

strongest line ZrK_{α_1} of the matrix in the second order has an almost complete interference with it. Thus, inspite of the second order diffraction and the pulse height discrimination, the ZrK_{α_1} from the matrix has considerable residual intensity so as to give a high background resulting in the poor signal to background ratio. Use of scintillation counter with coarse primary collimator and additional secondary auxiliary collimator, (Set B, Table I) gives the poorest signal to background ratio (0.09) among the Sets A-H of Table I. The use of flow proportional counter (Set A, Table I) improves the ratio to 0.19. This improvement is observed although flow proportional counter (F.C) has not been provided with the additional collimator which the scintillation counter (S.C) has. However, 'fine' primary collimator has been used with F.C. so as to compensate the collimation effect in the two cases (Sets A and B, Table I). With F.C., the net intensity and the sensitivity are quite high as can be seen from the Table, whereas from S.C. they are quite low. This is because the S.C. has a better counting efficiency for the unwanted interfering high energy ZrK_{α} radiation compared to the analytical radiation HfL_{α_1} . However, in the case of F.C. just opposite is the case. Analytical radiation HfL_{α_1} being of a longer wavelength is absorbed more efficiently in the detector's active volume, compared to the short wavelength undesirable second order matrix ZrK_{α_1} radiation. Thus the selective counting efficiency of F.C. for the analytical radiation helps in furthering discrimination against matrix radiation and helps electronic pulse height discrimination further, to improve the signal to background ratio, whereas

with the S.C. the selective higher counting efficiency for ZrK_{α} acts in the opposite direction and results in higher background and poorer signal to background ratio. In short, the use of P.C. with HfL_{α_1} and fine primary collimator gives the lowest detection limit (20 ppm) and the highest sensitivity $\left[\frac{38 \text{ counts per second change}}{100 \text{ ppm concentration change}} \right]$. Whereas the use of S.C. gives poorer detection limit (52 ppm) and inferior sensitivity $\left[\frac{3.3 \text{ c/sec change}}{100 \text{ ppm change in concentration}} \right]$.

Fig.2 gives the calibration curves for sets A & B, obtained from the measurements on the full set of standards. The spread of the plotted points from the mean lines is appreciable. Also, the slope of the lines is nowhere near 45° . Thus, inspite of the fact that these sets A & B of the parameters give high sensitivity and lower detection limits, their use for the analysis is not desirable. The performance of the set 'A' is fdr better compared to that of set 'B'. The plots clearly demonstrate that the high background against which the signals have been measured in both the cases, adversely affects the results.

7.2 The obvious way to improve the results is to reduce the background interference. One of the possible ways for reducing or eliminating the second order interference from the matrix radiation is to decrease the operating voltage of the x-ray tube. 17.995 kV is the excitation potential for the K-spectrum of Zr, whereas 11.3 kV only are required for exciting the L-spectrum of Hf. Thus by operating the tube at 20 kV and around, the primary continuum from it will excite the ZrK -spectrum weakly. However, the L-spectrum of Hf can be excited appreciably. The effect of reduction

of voltage of the primary x-ray tube on the measured x-ray fluorescence intensities from the three standards of nominal concentrations 100 ppm, 200 ppm and 500 ppm of HfO_2 in ZrO_2 is shown in Figs. 3(a) to 3(c).

Fig.3(a) gives the measured fluorescence intensity of $\text{HfL}\alpha_1$ (using flow counter) reduced to net counts/sec/mA tube current for the various voltages on the x-ray tube. The sharp fall in the count rates with reduction in voltage is clearly seen. However, this reduction in intensity is also accompanied by the reduction in the power of the x-ray tube. Fig.3(b) gives a more realistic picture. In this figure the intensities plotted, have been reduced to counts per sec. per kilowatt power of the x-ray tube. This is necessary in order to assess the effect of voltage vis-a-vis the tube current. In the former plot in Fig.3(a), the lowering of the voltage amounted to the lowering of the power of the x-ray tube, naturally resulting in lower count rates. However, when the count rates are calculated per kilowatt power of the x-ray tube, one observes the net effect of lowering the voltage vis-a-vis corresponding increased current. These plots in Fig.3(b), clearly show that initially the lowering of voltage (around 50 kV) results in a gradual fall in the intensity/kW power. However, below about 35 kV, the fall in the intensity is quite sharp. This clearly shows that the increase in the current (for maintaining the same power) cannot off-set the disadvantage resulting from the lowering of the voltage. This is because the fluorescence intensity in the initial stages (upto 3 V_c or so, where V_c is the excitation potential) increases as the square of the over-potential vis ($V-V_c$) but it increases linearly with the tube current. After about 3 V_c , it gradually

becomes a linear function of the overpotential also. Thus the sharp reduction in the fluorescence intensity of $\text{HfL } \beta_1$ due to the lowering of voltage may more than off-set the advantage of reducing the interference. Fig.3(c), the plot of the calculated peak count rate per kilowatt power against concentration of HfO_2 , for various voltages used, clearly demonstrates the effect. The increased slope of the calibration plots (sensitivity curves) clearly indicate the increased sensitivity ($\frac{\Delta I}{\Delta \text{conc}}$) obtainable by higher voltages. The sensitivity curves are almost parallel after 40 kV indicating that after 40 kV there is only a marginal advantage in the sensitivity by increasing the voltage. The increased background at higher voltages is obvious as seen from the graph.

Figs. 3(d) and 3(e) summarise the results obtained using $\text{HfL } \beta_{1,6}$ as the analytical line and F.C. as the detector. These results also substantiate the points discussed above.

7.3 Apart from the method discussed so far, the other way of avoiding the second order interference from the matrix radiation is to use $\text{HfL } \beta_2$ as the analytical line which is free from such an interference. Fig.4 gives the results obtained with $\text{HfL } \beta_2$ using S.C. as the detector and 'Fine' and 'Coarse' primary collimators. The relevant data are given under Sets E and F of Table I. $\text{HfL } \beta_2$ being a weak line required larger counting time. The coarse collimator as expected gives better sensitivity (5.4) compared to the fine collimator (1.3) although the signal to background ratio is reduced (.10) with coarse collimation as compared with the fine collimation (.15). The calculated detection limits with fine and coarse collimators are 166 ppm and 132 ppm respectively. These data indicate that

no advantage is accrued by the use of the weak $L\beta_2$ line of Hf, although it is free from matrix radiation interference. The net result being poorer detection limits, lower sensitivity and increased counting time, it is not desirable to use it for analytical purposes.

7.4 The two extreme cases of the almost complete interference and non-interference from matrix radiation have so far been discussed. The effect of the use of $HfL\beta_{1,6}$ (which has a partial interference) is shown in Fig.5. The relevant data are given in the set G of Table I. Flow counter has been used in this case because of its higher counting efficiency for the radiation ($HfL\beta_{1,6}$) diffracted in the first order, compared to that ($ZrK\beta_2$) diffracted in the second order. This helps in furthering the discrimination of the undesirable matrix radiation (See also discussion part concerning set 'A'). $HfL\beta_{1,6}$ though somewhat weaker compared to $HfL\alpha_1$ has only the second order interference from the very weak $ZrK\beta_2$ line of the matrix. Thus weak intensity of interfering radiation, discrimination due to the preferential counting efficiency of F.C. for $HfL\beta_{1,6}$, electronic pulse height discrimination and poor reflectivity of $LiF(200)$ in the second order - all these factors favour the reduction of the background and the improvement of the signal to noise ratio when set 'G' is used. The signal to background ratio for this combination of parameters is the highest (0.28) and the sensitivity is also quite appreciable (14.2). The calculated detection limit is 29 ppm which is comparable with the best (20 ppm) obtained in the present studies. From the plot (Fig.5), it is further seen that all the points lie on the straight line with practically no spread. Thus the precision of the

determination of HfO_2 is almost the same as the precision of intensity measurements (given by the standard counting error). This set of parameters is thus the optimum for the determination of the traces of HfO_2 in ZrO_2 .

7.5 A further reduction in interference of second order matrix radiation may be expected by measuring $\text{HfL } \beta_{1,6}$ after the second order diffraction from $\text{LiF} (200)$. The matrix radiation $\text{ZrK } \beta_2$ in this case will be diffracted in the fourth order. Thus electronic pulse height discrimination will be more effective. Further, the increased dispersion and resolution (in the second order) and reduced reflectivity of LiF in the fourth order, may eliminate the interference altogether. The results obtained with this set of parameters are given in Fig.6 and the relevant data in set 'H' of Table I. There is no improvement in the signal/background ratio which is decreased to 0.21 compared to 0.28 in the former case (set G). The obvious conclusion is that the background at $\text{HfL } \beta_{1,6}$ is not entirely due to $\text{ZrK } \beta_2$ radiation but from other sources also. The loss of intensity because of second order diffraction necessitates the increase in the counting time, otherwise it results in inferior sensitivity (1.6) and detection limit (104 ppm). However, the only impressive feature of this set, vis-a-vis the other ones is that all the experimental points lie on a straight line with practically no spread as in the previous case (set 'G'), indicating that the precision of the determination is practically the same as the precision of the intensity measurements.

8. CONCLUSION

Traces of hafnia in high purity zirconia can be determined with high precision and accuracy using the x-ray fluorescence spectrometric technique. Among the various combinations of the variable experimental parameters studied, the set - $HfL \beta_{1,6}$ analytical line, fine collimation and gas flow proportional detector - gives the optimum performance, when used with the fixed parameters - Philips semiautomatic x-ray spectrometer PW 1220. LiF (200) analysing crystal in the I order, high power on the x-ray tube (60 kV, 35 mA, W target) with electronic pulse height discrimination using amplifier/analyser of the standard electronic panel (PW 1360).

ACKNOWLEDGEMENTS

The authors express their sincere thanks to Dr. N.A. Narasimhan, Head, Spectroscopy Division, BARC for his interest and encouragement. One of us (Jura Mohammad Qurbani) is also thankful to the Department of Atomic Energy, Government of India for the grant of a fellowship to him under the Colombo Plan. We are also thankful to Shri T.R. Saranathan for reading the manuscript.

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1. A. Brookes and A. Townshend:
Analyst 95, 531 (1970).

Table I

Fixed parameters

- (i) Target of the x-ray tube - tungsten.
- (ii) Pulse height discrimination using single channel analyser and automatic pulse height selection mechanism.
- (iii) Sample spinner - 'ON'.
- (iv) Path - vac.

<u>Variable parameters / Sets</u> →	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
I-ray tube voltage (kV)	60	60	(20-50) Various	(20-50) Various	60	60	60	60
I-ray tube current (mA)	35	35	Various	Various	35	35	35	35
Analyzing crystal	LIF I (200)	LIF I (200)	LIF I (200)	LIF I (200)	LIF I (200)	LIF I (200)	LIF I (200)	LIF II (200)
Analytical line of Hf	$L\alpha_1$	$L\alpha_1$	$L\alpha_1$	$L\beta_{1,6}$	$L\beta_2$	$L\beta_2$	$L\beta_{1,6}$	$L\beta_{1,6}$
Wavelength (Å.U)	1566.33	1566.33	1566.33	1371.25	1323.64	1323.64	1371.25	1371.25
2 θ angle (degrees)	45.97	45.97	45.97	39.94	38.50	38.50	39.94	86.16
Collimator	Fine	Coarse	Fine	Fine	Fine	Coarse	Fine	Fine
Additional auxiliary collimator	No	Yes	No	No	Yes	Yes	No	No
Detector	P.C.	S.C.	P.C.	P.C.	S.C.	S.C.	P.C.	P.C.
Voltage	1680	1000	1680	1680	1000	1000	1680	1680
<u>Analyser settings:</u>								
Base line (div)	250	250	250	250	250	250	250	250
Window (div)	250 x 1	350 x 1	250 x 1	250 x 1	350 x 1	350 x 1	250 x 1	250 x 1
Counting time (sec.)	60	60	100	100	200	100	100	60
Reference Fig. No.	2	2	3(a),(b), (c)	3(d),(e)	4	4	5	6
<u>Average count rates (per sec.)</u>								
Total peak intensity (500 ppm std.)	2039	1103			42.5	129.3	425	59.7
% std. dev./ <i>(n)</i> *	0.34/(4)	0.15/(4)			1.2/(4)	1.4/(4)	0.75/(11)	1.2/(10)
Blank	1723	1011			37	117.0	331	49.5
% std. dev./ <i>(n)</i> *	0.67/(4)	1.5/(8)			1.4/(7)	1.2/(7)	1.3/(34)	0.96/(35)
Net intensity (500 ppm std.)	316	92			5.5	12.3	94	10.2
% std. dev.	4.3	17.0			12.1	18.1	6.1	7.1
<u>Signal/background ratio</u>	0.19	0.09			0.15	0.10	0.28	0.21
<u>Sensitivity</u> $\frac{\Delta(c/sec.)}{\Delta(100 ppm)}$	38	3.3			1.3	5.4	14.2	1.6
<u>Calc. detection limit (ppm)</u>	20	52			166	132	29	103

* Values given in bracket along with std. deviations show the number of readings 'n' used for calculating std. deviation.

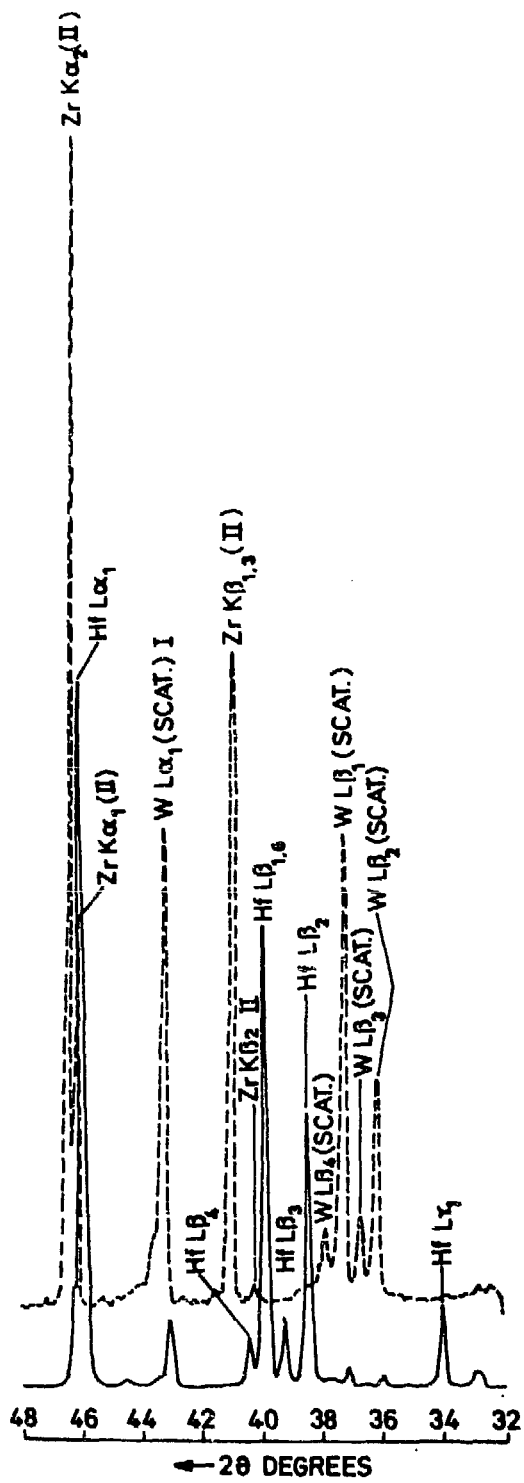


FIG.1.

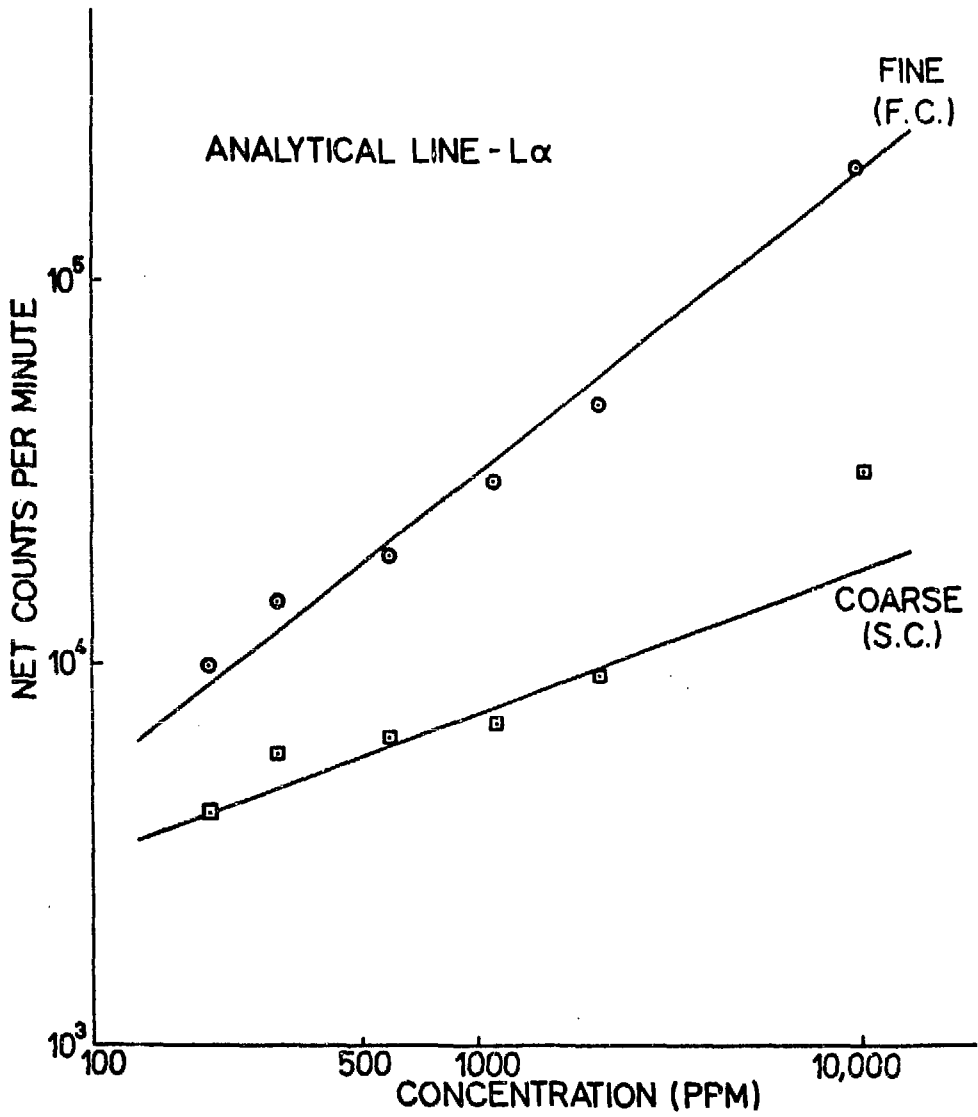


FIG. 2.

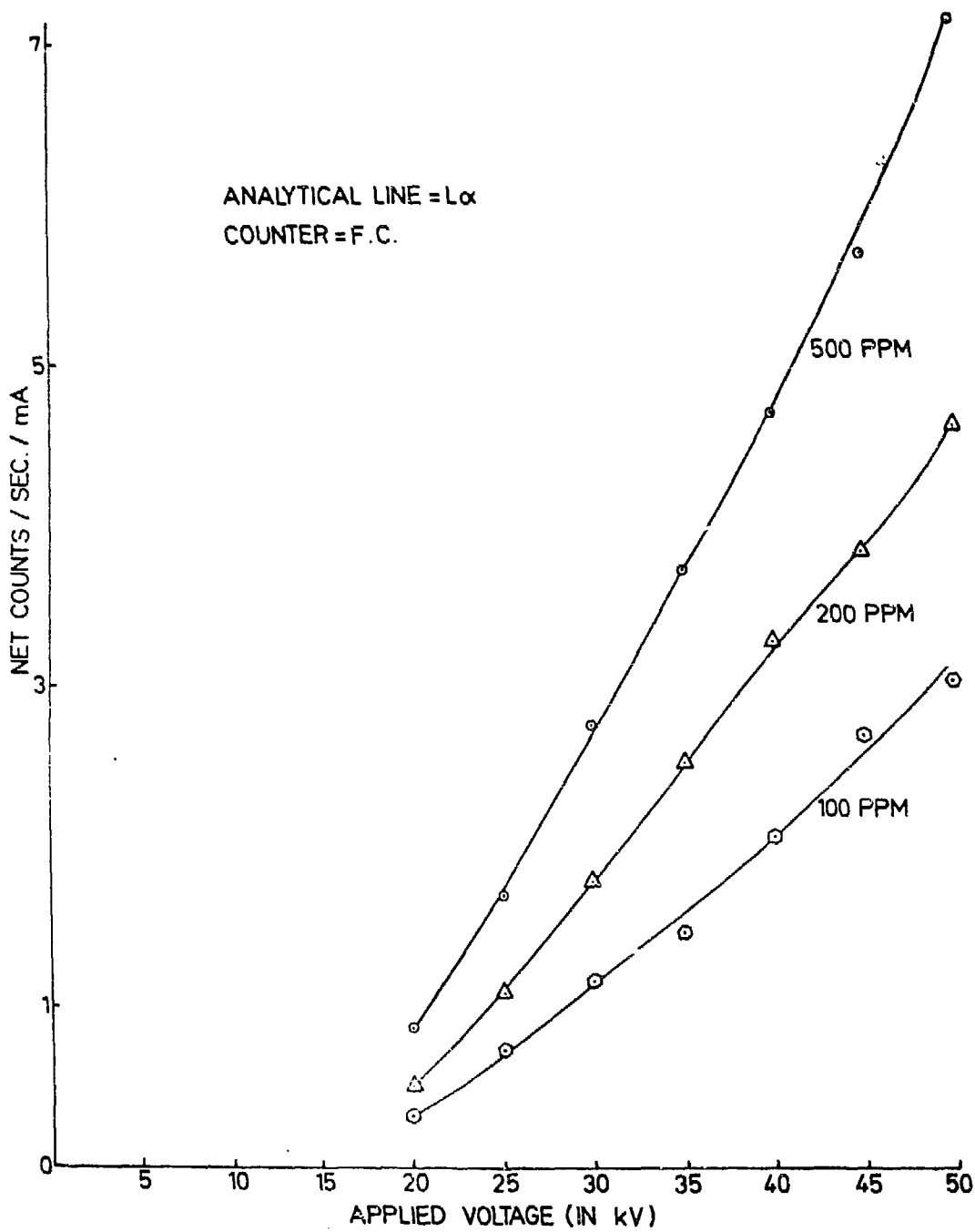


FIG. 3(a)

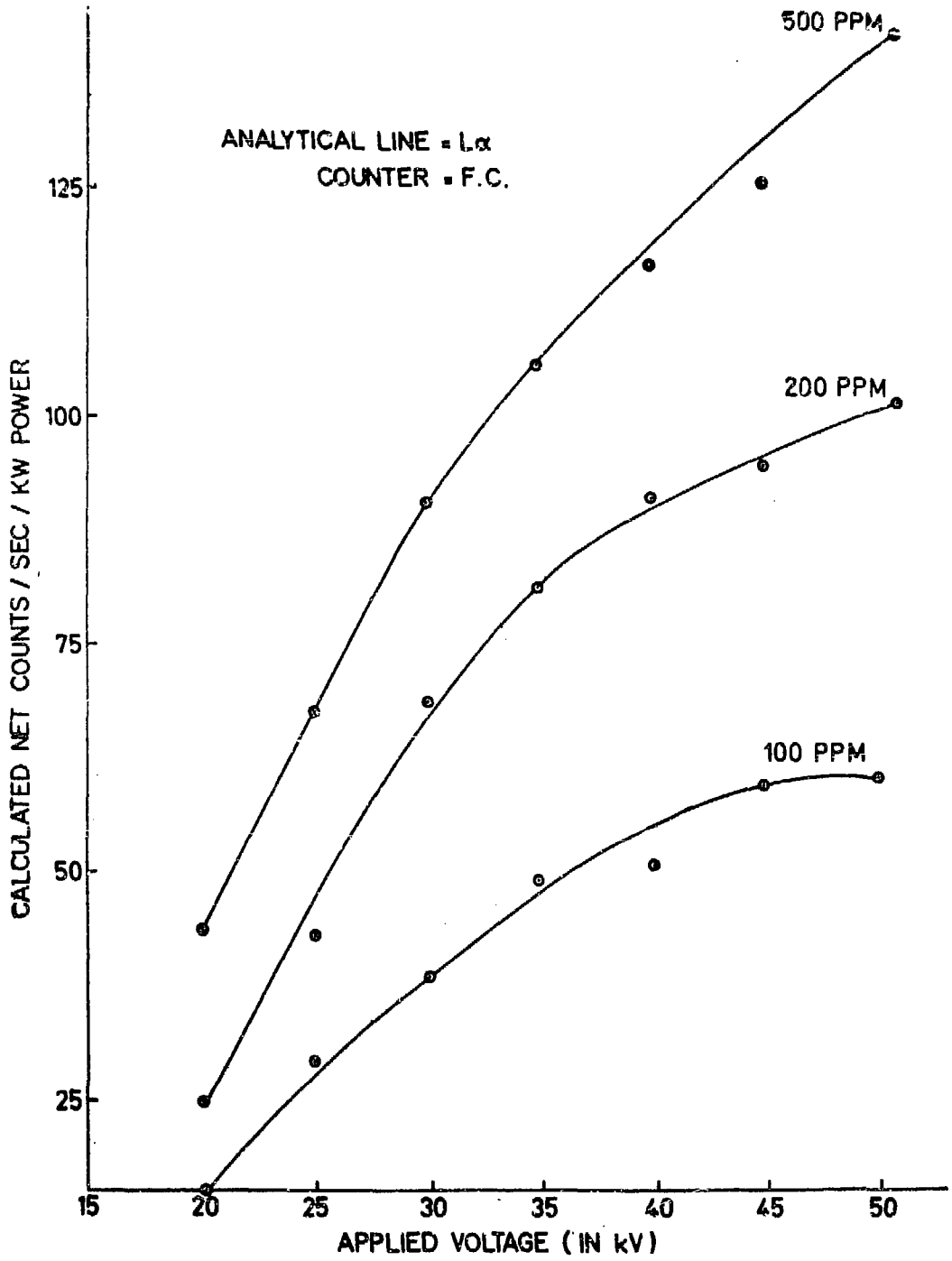


FIG. 3(b)

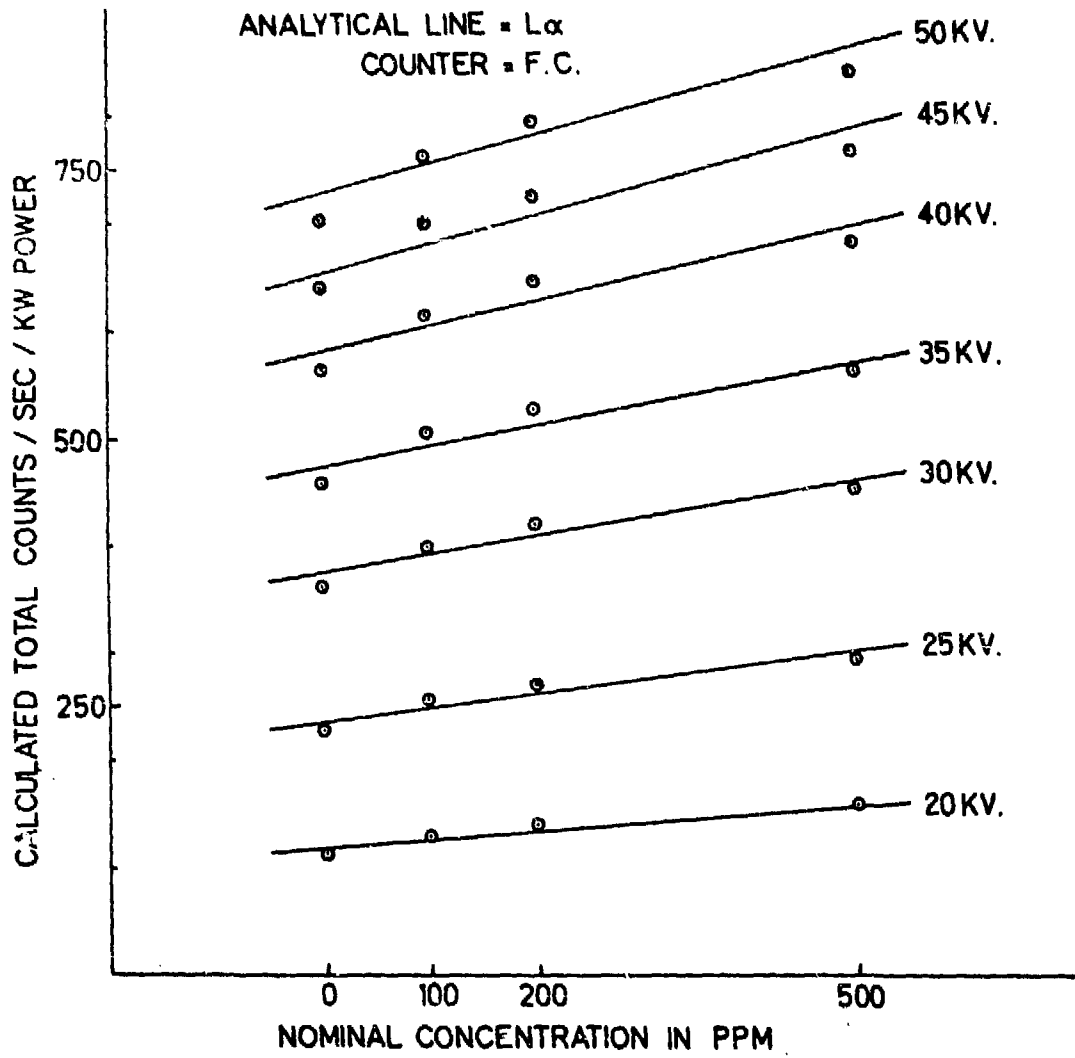


FIG. 3(c)

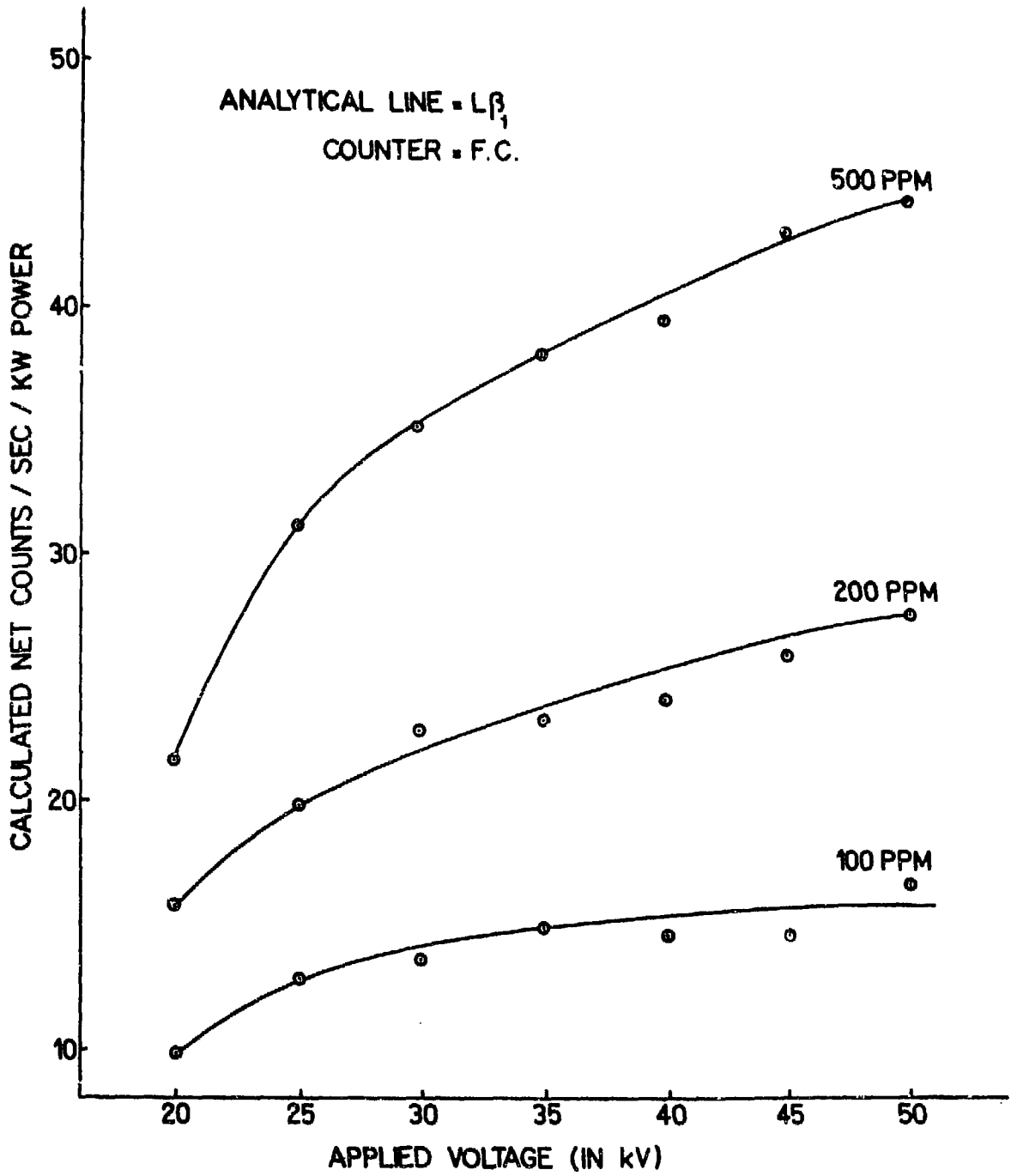


FIG.3(d)

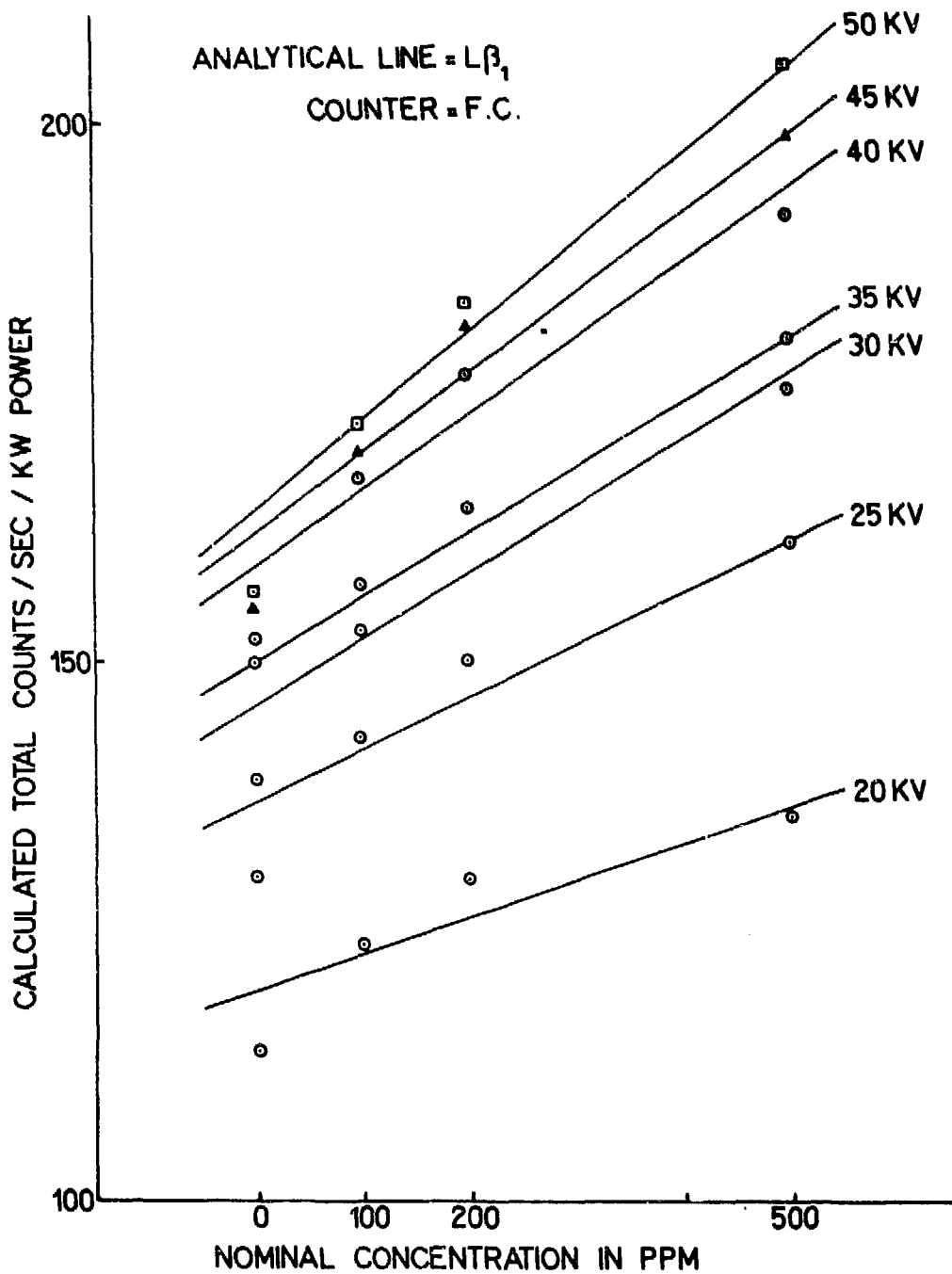


FIG.3(e)

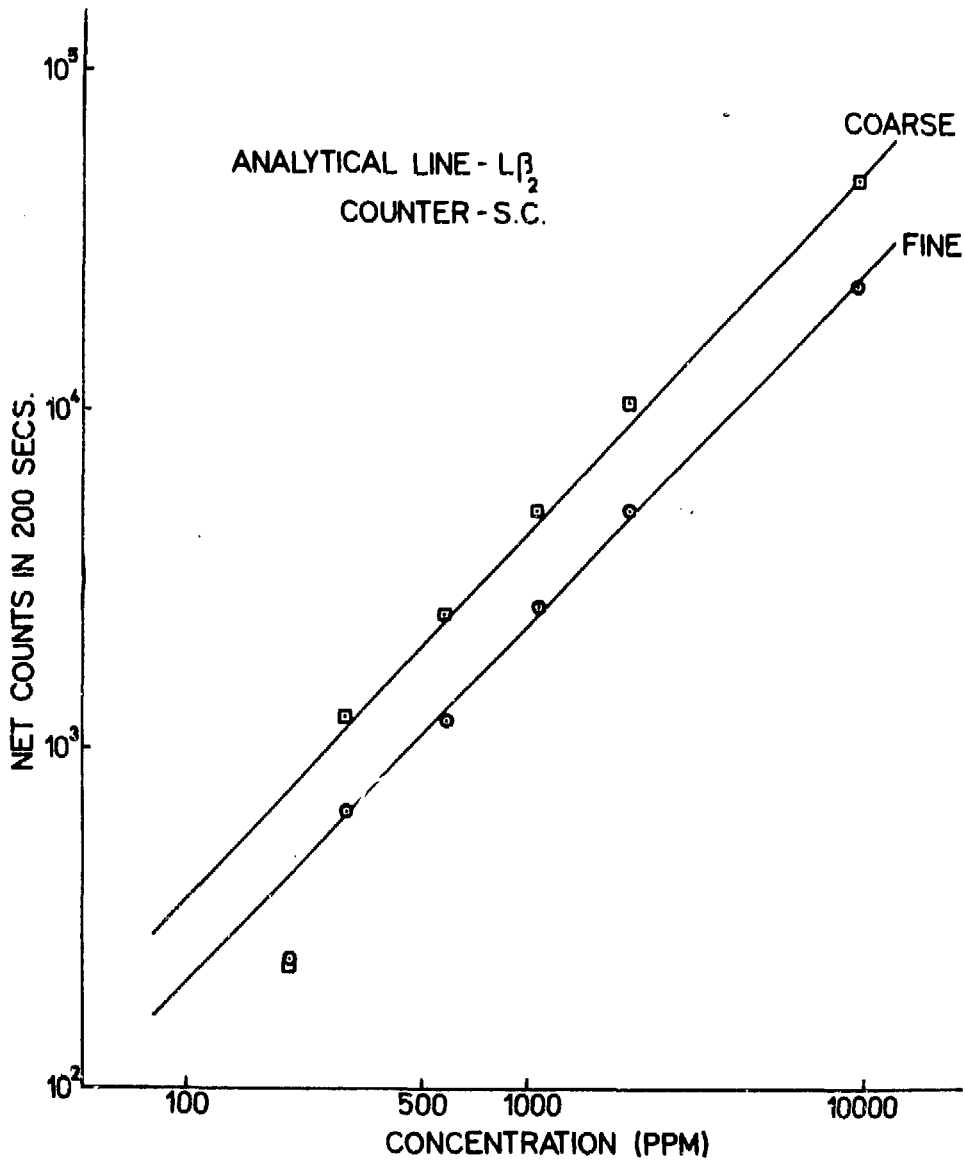


FIG. 4.

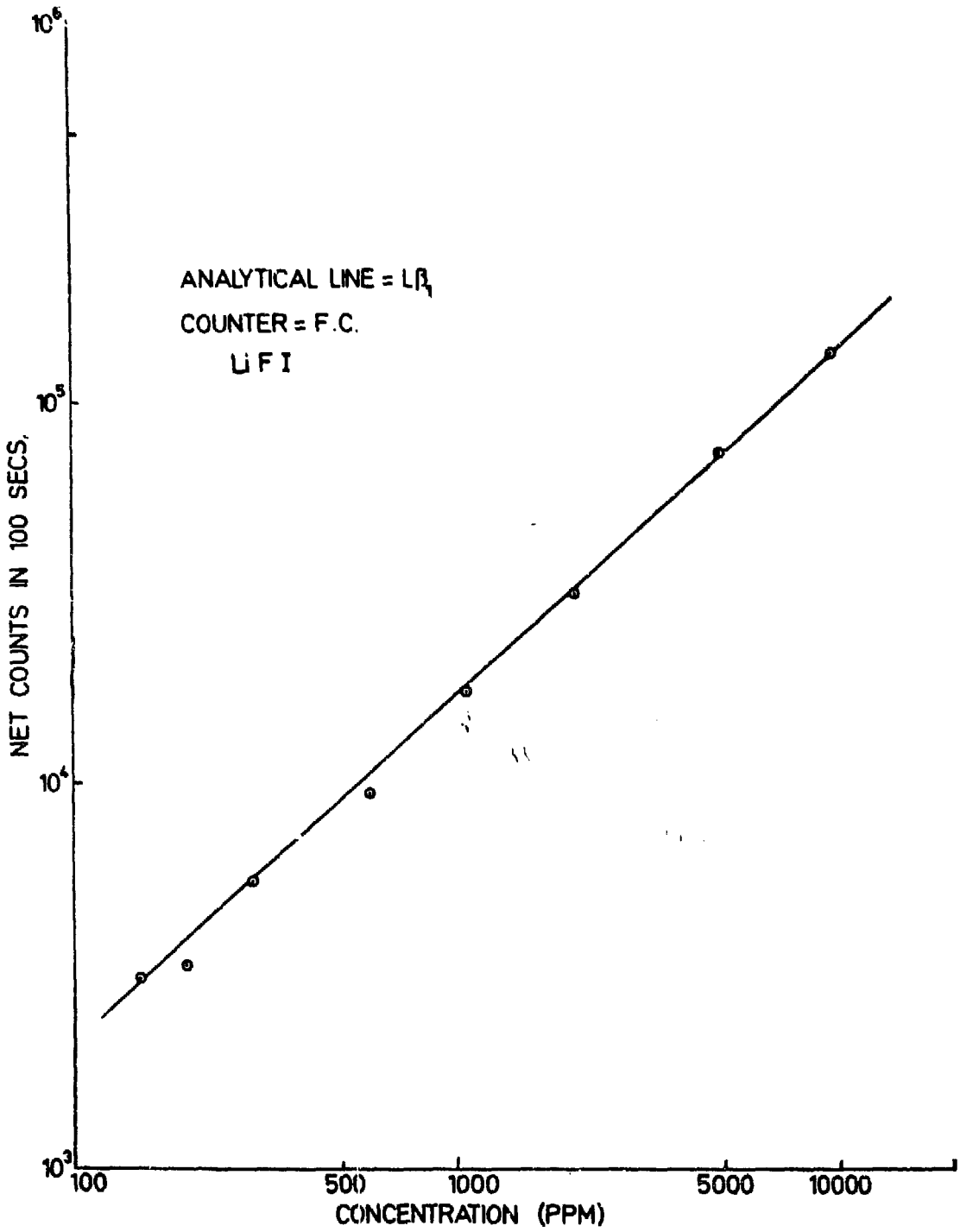


FIG.5.

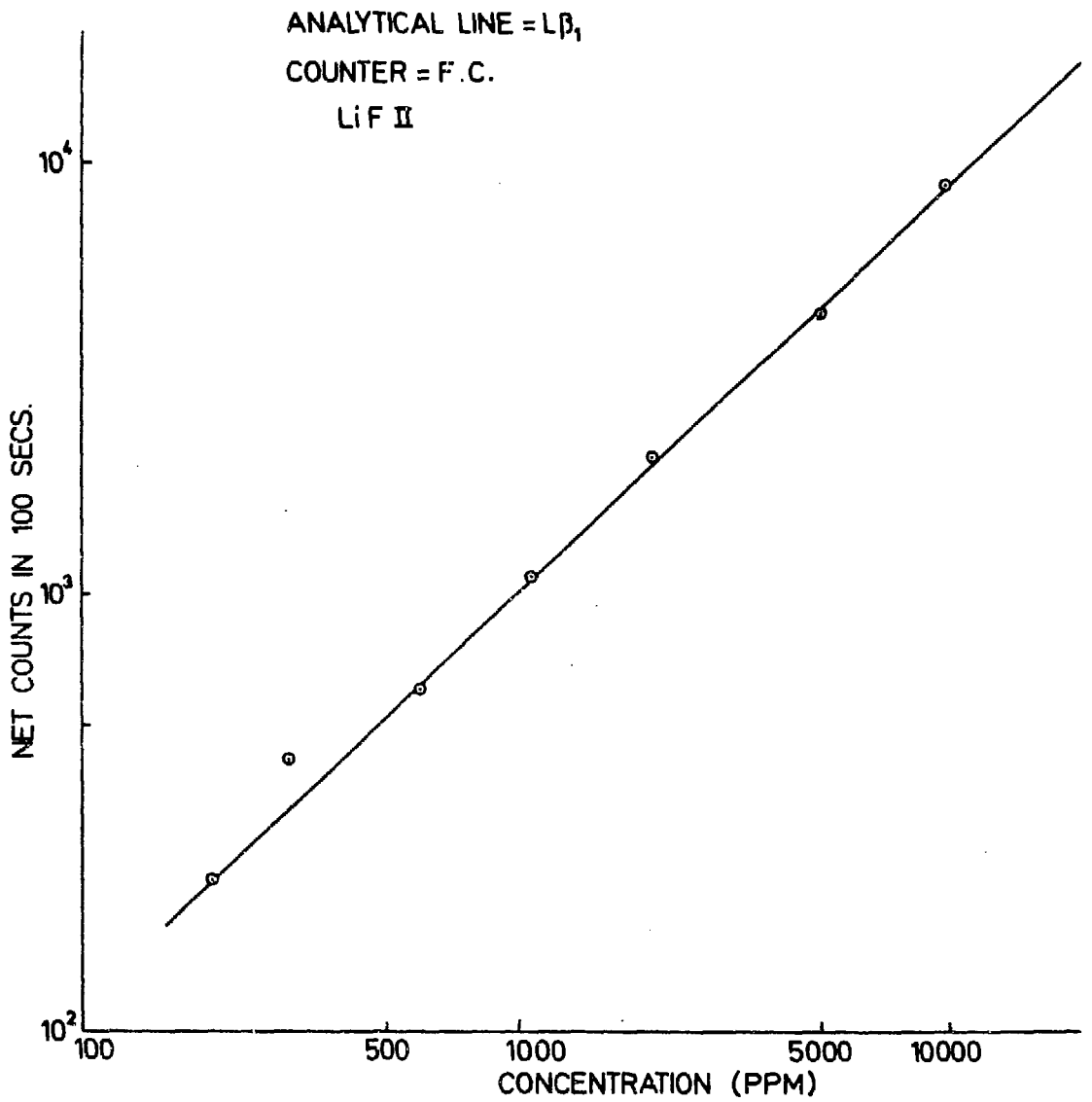


FIG. 6.

