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PREPARATORY STUDIES FOR THE ON-LINE DETERMINATION OF ZINC
CONTENT IN ZINC ORE SLURRIES BY RADIOISOTOPE EXCITED X-RAY
FLUORESCENCE

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DETERMINATION OF ZINC CONTENT IN ZINC
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VORUNTERSUCHUNGEN ZUR ON-LINE BESTIMMUNG VON ZINK IN
ZINKERZTRÜBE MITTELS RÖNTGENFLUORESZENZANALYSE.

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KURZFASSUNG

Laboruntersuchungen in Hinblick auf die Bestimmung von Zink in Zinkerzaufschlämmungen (Trüben) wie sie bei der Aufbereitung von Zinkerzen anfallen, wurden mit Hilfe der Röntgenfluoreszenzanalyse mittels Radioisotopen durchgeführt. Neben Untersuchungen des Matrixeffektes an trockenen Proben wurden Messungen an einem Testkreislauf im Labor durchgeführt. Die Ergebnisse zeigen, daß unter den gegebenen Bedingungen für die Zinkkonzentration in der Trübe eine Meßgenauigkeit von 0,05 % Zink erreicht werden kann. Eine semi-empirische Formel zur Interpretation der Meßergebnisse wird abgeleitet.

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ABSTRACT

Laboratory tests were carried out to prove the feasibility of determination of Zn-content in zinc ore slurries by isotope excited x-ray fluorescence. Matrix effects were investigated on dry samples. A slurry testloop was built and measurements on slurries were made. The results indicated that the measurement on Zn in ore slurries can be made with a precision of 0,05 % Zn. A working equation for interpretation of the measurements is derived.

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1. SCOPE

The purpose of the research done under this contract was to determine the feasibility of a low-cost X-ray fluorescence (XRF) analysis system for on-line determination of ore content in mineral slurries employing a radioisotope source for excitation of characteristic X-rays. The research was aimed at single-element determination of one major element in an otherwise fairly constant matrix. The application in mind is the determination of Zn-concentration in the tailings from the flotation plant of an Austrian zinc mine.

In the first year of the project research was carried out up to the point of laboratory tests of the proposed equipment using recirculation of slurries in a test loop including a measuring cell. The results of these tests are given in the report.

2. BASIC CONSIDERATIONS.

In XRF technique the characteristic X-rays of one or more elements contained in the sample or stream to be analysed are excited by irradiation with a primary source of radiation, e.g. an X-ray tube or a radioisotope source. The intensity I_a of fluorescent X-rays emitted by the element a which is contained in the sample with a weight fraction x_a is given by the general equation (1):

$$I_a = kI_0 \frac{w \cdot \tau \cdot x_a}{\sum_i (\mu_i' + \mu_i'') \cdot x_i} \cdot \left[1 - \exp - \left(\sum_i (\mu_i' + \mu_i'') x_i m \right) \right] \quad (1)$$

in which the following symbols are used:

- k ... overall geometrical and detector efficiency
- I_0 ... incident primary photon flux
- w ... fluorescence yield of the element a for the X-ray under consideration
- τ ... photoelectric absorption coefficient of the element a at the energy of incident photons
- μ_i' ... total absorption coefficient of element i in the sample at the energy of incident photons
- μ_i'' ... total absorption coefficient of element i in the sample at the energy of fluorescent X-rays
- x_i ... weight fraction of element i in the sample
- Y_A ... total mass per unit area of the sample.

For the purpose of the present investigation the sample may be considered infinitely thick so that equation (1) can be reduced to

$$I_a = kI_0 \frac{w \cdot \tau \cdot x_a}{\sum_i (\mu_i' + \mu_i'') x_i} \quad (2)$$

which may be considered as the working equation for the evaluation of all measurements. All results of measurements can be considered valid only if they may be interpreted by equation (2) or a formula which is derived from it.

XRF techniques have been applied to mineral analysis in the past [1-5] . A list of applications in reference [4] shows several feasibility studies using different techniques for on-stream analysis of mineral slurries. However, from all of them only

the immersed probes using scintillation detectors have reached industrial level and more widespread use at least in one country [2,3]. This is largely due to the impact of large systems developed by the industry already present in the field of dispersive XRF using X-ray tubes [6,7]. In order to compete against this type of expensive equipment, sophisticated energy-dispersive systems using solid-state detectors were developed [8]. All of these systems, many of them equipped with a small computer, allow multi-element analysis of several sample streams which quite often is not required in smaller plants. The submersible probes developed in Australia show the need for simpler and less expensive equipment.

Another approach to the development of a low-cost analysis system is the use of a proportional counter tube for energy dispersion. Unless there is the necessity to discriminate neighbour elements of the periodic system, the energy resolution of the proportional counter is sufficiently good to obtain high sensitivities. The main objection against proportional counters in the past was their instability due to changes in the gas amplification due to temperature, count rate drift and ageing. Since the application of automatic gain control to proportional counters has become common [9], these detectors have reached a stability level which makes them useful tools for on-line applications even under exacting industrial conditions [10]. In the present investigation the feasibility of a simple measuring system based upon a radioisotope source for excitation of X-rays and a stabilised proportional counter for detection was studied.

3. MEASURING EQUIPMENT

The detection system used in all experiments consisted of an annular ^{241}Am source with Be window (Amersham source type AMC 8706) with a source strength of 100 mCi and a proportional

counter with 1 atm Ar/CO₂ filling and a 1 inch diameter Be entrance window. (Reuter Stokes RSG 61). The proportional counter was coupled to a charge sensitive preamplifier and main amplifier. The high voltage supply was obtained from the closed loop gain control system. The pulses from the 60 keV gamma rays from the ²⁴¹Am source detected in the proportional counter are continuously monitored via a discriminator and compared digitally to a reference frequency [11]. If the Am count rate equals the reference frequency on an average basis a constant high voltage is generated by a DC/DC converter. A decrease of the Am count rate with respect to the reference frequency causes an increase of the high voltage thus compensating the drift that caused the initial count rate shift. The opposite action is taken if the Am count rate is increased. Theory and details of this gain control system are given in references [9, 11]. By the use of this gain control system for the proportional counter long term stability of the Zn-K-X-ray peak count rate of 0.1 % could be achieved.

Spectral analysis was made by a Canberra Model 8100 multichannel analyser and later on when routine measurements were made, by a single channel analyser set to measure the Zn-K-X-ray peak.

4. MINERAL AND ECONOMIC SITUATION

The slurries which are to be measured primarily are the tailings from a flotation plant for lead and zinc ores. The mill feed contains typically 2.25 % lead and 6.25 % zinc on a yearly average. Ore concentrations in the tailings are to be expected in the order of 0.5 % lead, 0.5 to 1.5 % zinc and approximately 1.0 % iron in the form of pyrite. The matrix consists of a mixture of limestone and dolomite [12]. The raw ore is ground in a pebble mill with classifier. The flotation feed therefore has a grain size distribution with 60 % of the material less than 60 micron.

The throughput of the flotation plant is 320.000 metric tons of raw ore per year. At present only visual analysis of ore content in the tailings is made by the plant operators. Chemical analysis is made on one average sample per shift. Relatively large variations of zinc content are observed in the tailings therefore. Assuming that continuous on-line measurement could improve recovery from the tailings by only 0.1 % - which seems to be a rather conservative estimate - the output of the plant could be improved by 320 metric tons of zinc corresponding to an additional revenue of \$ 200.000,-- per year at the present cost of \$ 605,-- per metric ton of zinc.

5. LABORATORY MEASUREMENTS ON DRY SAMPLES

Due to the presence of varying concentrations of lead and iron in the material which is to be analyzed, it was necessary to investigate the matrix effects which might affect the measurement of zinc concentration. For this purpose measurements on dry powder samples were carried out. Dry samples of tailings were obtained from the flotation plant. The samples were measured in vials with 25 micron thick mylar foil bottom. The zinc content of these samples ranged from 1,6 % to 3.45 % zinc.

At first samples were prepared containing 1 %, 1.5 % und 2 % iron, respectively, by admixture of iron oxide to the regular samples. Measurements of the zinc X-ray count rates on these samples were made. The results are given in table 1 and are shown graphically on figure 1. Regression analysis of the data showed no significant difference between sets of data from samples with different iron content. In addition, it is obvious that the relationship between count rate and zinc content is linear.

A similar investigation was made concerning the influence of lead content of the sample on the zinc count rate. Samples with lead concentrations of 0.5 % and 1.0 %, respectively were prepared and measured. Results are given in table 2 and are plotted in figure 2. Regression analysis of the data showed a slight influence of lead content on the zinc X-ray count rate. It is indicated, that a 0.4 % change in the slope of the calibration curve occurs for a 0.1 % change in lead content. Even at a maximum expected variation in lead content of 0.5 % lead this leads to an error of the zinc determination of 0.02 % zinc at a level of 1 % zinc. This error is further reduced in the case of the actual slurry measurement since a further dilution of the material takes place, thus further diminishing any matrix effects.

From the measurement of dry samples it could be concluded that no matrix correction would be necessary for slurry analysis. A straightforward measurement of the intensity of zinc K-X-rays and a correction for solids content of the slurry via a density measurement should enable reliable determination of zinc concentration in the slurries.

Following standard methods in determining sensitivity and precision one obtains from the calibration curves for dry samples a sensitivity of 0.03 % zinc and a precision of 0.03 % zinc at 1 % zinc. Both values are based on three standard deviations for a one minute counting time.

6. LABORATORY TEST LOOP FOR SLURRY MEASUREMENTS.

A simple test loop was built for laboratory measurement on slurries. A schematic diagram of the test loop is shown in figure 3. It consists of a measuring flow cell (Fig. 4) and a circulation pump connected via plastic hose. The gamma density measurement also shown in figure 3 was added later for determination of solids content. The measuring cell was

designed in order to obtain laminar flow through the measuring area of the cell. This was achieved by proper shaping of the inlet and outlet sections of the cell and by maintaining the same cross section in the measuring area. The cell window is a teflon coated beryllium disc 50 mm in diameter, 0.3 mm thick. The rigidity of Be is thus combined with the resistance against corrosion and wear of teflon. This combination turned out to be very favourable in long term tests. The test loop was operated using slurries of up to 50 % solids and at flow rates of up to 2 litre/sec corresponding to a linear velocity of 4 m/sec. In this initial setup of the test loop the X-ray flow cell was mounted in a horizontal section of the loop. In this configuration a dependence of the Zn-X-ray count rate on the velocity of the slurry in the loop was observed. Therefore the setup was changed so that the flow through the cell is in vertical direction. No such dependence on the velocity was observed after that change had been made. It was concluded that the dependence was caused by sedimentation rather than by turbulence.

Attached to the flow cell was the measuring head consisting of the ^{241}Am source and the proportional counter that had already been used in the measurements on dry samples.

For the measurements with the test loop ore samples of known zinc concentration were used. Actual dried tailing samples were obtained for that purpose from the plant. The zinc concentration ranged from 0.8 % to 4.8 %. Weighed amounts of the material were filled into the test loop and mixed with water. After a few revolutions in the loop complete mixing was achieved and the solid material was distributed evenly in the slurry. The solids content was varied from 100 g/l to a maximum of 800 g/l in steps of 100 g/l. The zinc count rate was measured. The results are given in figure 5. At first it was intended to measure the

slurry density by observing the intensity of compton back-scattered primary 60 keV gamma rays from ^{241}Am . However, it was found that the dependence of the backscatter peak intensity on slurry density was not sufficient for accurate density determination. In addition, dependence of backscatter count rate on varying zinc concentrations was experienced and this method was therefore abandoned. A simple ^{137}Cs density gauge was then used which performed well. A 3 mCi source and a radiation path of 30 cm length was used. At the other side a 1 inch diameter by 1 1/2 inch NaJ crystal was used for detection of the gamma rays. A calibration curve for this setup is shown in figure 6.

From figure 5 it can be seen that all measurements for the same solids content of the slurry are on one linear calibration curve. The slope for different solids contents is different, however. All different calibration lines intersect in one point on the y-axis. Statistical accuracy of the individual points is always better than 0.2 %.

An evaluation of the measurements was tried to make in accordance with equation 2. For reasons of simplicity the entire slurry system may be considered to consist of three fractions: zinc, limestone matrix and water. In that case equation 2 can be rewritten if the following simplifications and symbols are used:

s solids content of the slurry

x_{Zn} .. zinc concentration in the solids

$x_{\text{m}} = 1 - x_{\text{Zn}}$... concentration of matrix elements in solids

$\mu_{\text{Zn}} = \mu_{\text{Zn}}' + \mu_{\text{Zn}}''$ the overall absorption coefficient for Zn

$\mu_{\text{m}} = \mu_{\text{m}}' + \mu_{\text{m}}''$ the overall absorption coefficient for the matrix

$\mu_{\text{w}} = \mu_{\text{w}}' + \mu_{\text{w}}''$ the overall absorption coefficient for water

$$I_{Zn} = kI_o \frac{w \cdot x_{Zn} \cdot s}{[\mu_{Zn} x_{Zn} + \mu_m (1-x_{Zn})] \cdot s + \mu_w (1-s)} \quad (3)$$

$$I_{Zn} = kI_o w \frac{x_{Zn} \cdot s}{s \cdot [x_{Zn} (\mu_{Zn} - \mu_m) + (\mu_m - \mu_w)] + \mu_w} \quad (4)$$

The linear dependence of the zinc X-ray intensity on the zinc concentration shown clearly by the results indicates, that the term containing the zinc concentration x_{Zn} in the denominator of equation (4) can be neglected due to the small concentrations involved and since only the difference of the overall absorption coefficients for zinc and the matrix appears as coefficient. Therefore (4) can be further reduced to

$$I_{Zn} = kI_o w \frac{x_{Zn} \cdot s}{(\mu_m - \mu_w) \cdot s + \mu_w} \quad (5)$$

or in a more general form

$$I_{Zn} = K \cdot \frac{s}{s + a} \cdot x_{Zn} \quad (6)$$

In practice, of course, there is always some background count rate N_o which must be considered in fitting the data. The general form of equation (6) for practical application is therefore

$$I_{Zn} = K \cdot \frac{s}{s + a} \cdot x_{Zn} + N_o \quad (7)$$

The data from 40 individual measuring points were fitted by regression analysis to the expression of equation (7). The solid lines in figure 5 are the result of this fit. It is evident that the fit is excellent over the entire range of zinc concentrations and solids contents used in the tests. The numerical expression for the curve fit is given below:

$$I_{Zn} = 1165 \cdot \frac{s}{s + 266,7} \cdot x_{Zn} + 2310 \quad (8)$$

The test measurement was repeated under slightly modified conditions. The count rates were again fitted and similar results were obtained.

The fact that the zinc count rates from the slurry measurement can be fitted to a semi-empirical mathematical equation is rather important for two reasons. First, as mentioned in chapter 2, the ability to fit the data to an expression that can be derived from general theory indicates that the results obtained are meaningful in the sense that they are generally applicable. Second, it is rather important to have a working equation if one considers to apply a measurement to on-line practice. The existence of a working equation enables the direct conversion of the measurements into the actual figures necessary for the plant operation, in this case to percent zinc concentration.

For complete conversion of the data obtained from the measurement to zinc concentration it is necessary to use the result of the density measurement in addition to the zinc X-ray measurement. The calibration curve for the density - or solids content - is truly exponential which was achieved by proper shielding of source and detector from scattered radiation. The intensity I_d of the gamma radiation as a function of

solids contents in g/l in the given setup is:

$$I_d = 875.3 \exp (-0.001362 s) \quad (9)$$

By combination of (8) and (9) one is able to express the zinc concentration x_{Zn} as a function of X-ray count rate I_{Zn} and gamma count rate I_d :

$$x_{Zn} = (I_{Zn} - 2310) \cdot \frac{s + 266.7}{1165 s}$$

$$s = - \frac{1}{0.001362} \ln (I_d / 875.3) \quad (10)$$

This simple equation can be easily computed electronically by a calculator chip to that direct indication of zinc content can be made.

An evaluation of statistical count rate errors shows, that with the count rates obtained in the test setup a statistical error better than 0.02 % zinc can be obtained for a typical solids content of 300 g/l. Considering additional error due to drift etc., a total precision of better 0.05 % can be obtained with the proposed equipment.

7. CONCLUSION

By the current investigation it could be shown that zinc content in tailings can be measured by X-ray fluorescence based on a ^{241}Am radioisotope source and a proportional counter as energy dispersive analysis system. Laboratory tests of the system resulted in the derivation of a working equation including a correction for solids content of a slurry. The proposed equipment was operated in the laboratory in a closed loop for which data were collected.

In the next step on-line tests of the measuring equipment should be carried out directly in the flotation plant in order to study the function under plant conditions.

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TABLE 1

INFLUENCE ON IRON CONTENT ON ZINC X-RAY COUNT RATE

Sample No.	% Zinc	% Iron	Zinc-K-X Count Rate CPM
1	1,60	1,00	53 720
1 a	1,59	1,50	52 830
1 b	1,58	1,99	53 800
2	1,98	1,00	59 600
3	2,35	1,00	66 500
3 a	2,34	1,50	66 400
3 b	2,33	1,99	66 500
4	2,73	1,00	74 200
5	3,10	1,00	81 900
6	3,48	1,00	87 400
6 b	3,45	1,98	86 200

TABLE 2

INFLUENCE OF LEAD CONTENT ON ZINC X-RAY COUNT RATE

Sample No.	% Zinc	% Lead	Zinc-K-X Count Rate CPM
1 x	1,59	0,50	37 981
2 x	1,97	0,50	44 218
3 x	2,34	0,50	49 717
4 x	2,72	0,50	57 778
5 x	3,10	0,50	62 508
6 x	3,48	0,50	67 982
1 y	1,58	1,00	37 114
2 y	1,96	1,00	44 966
3 y	2,33	1,00	49 886
4 y	2,71	1,00	57 307
5 y	3,08	1,00	61 399
6 y	3,46	1,00	68 784
1	1,60	0,10	37 777
2	1,98	0,18	43 636
3	2,35	0,25	49 232
4	2,73	0,33	55 017
5	3,10	0,40	61 707
6	3,48	0,48	66 875

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- Fig. 6 Calibration curve for ^{137}Cs density measurement.

$\times 10^3$ CPM
ZINC K

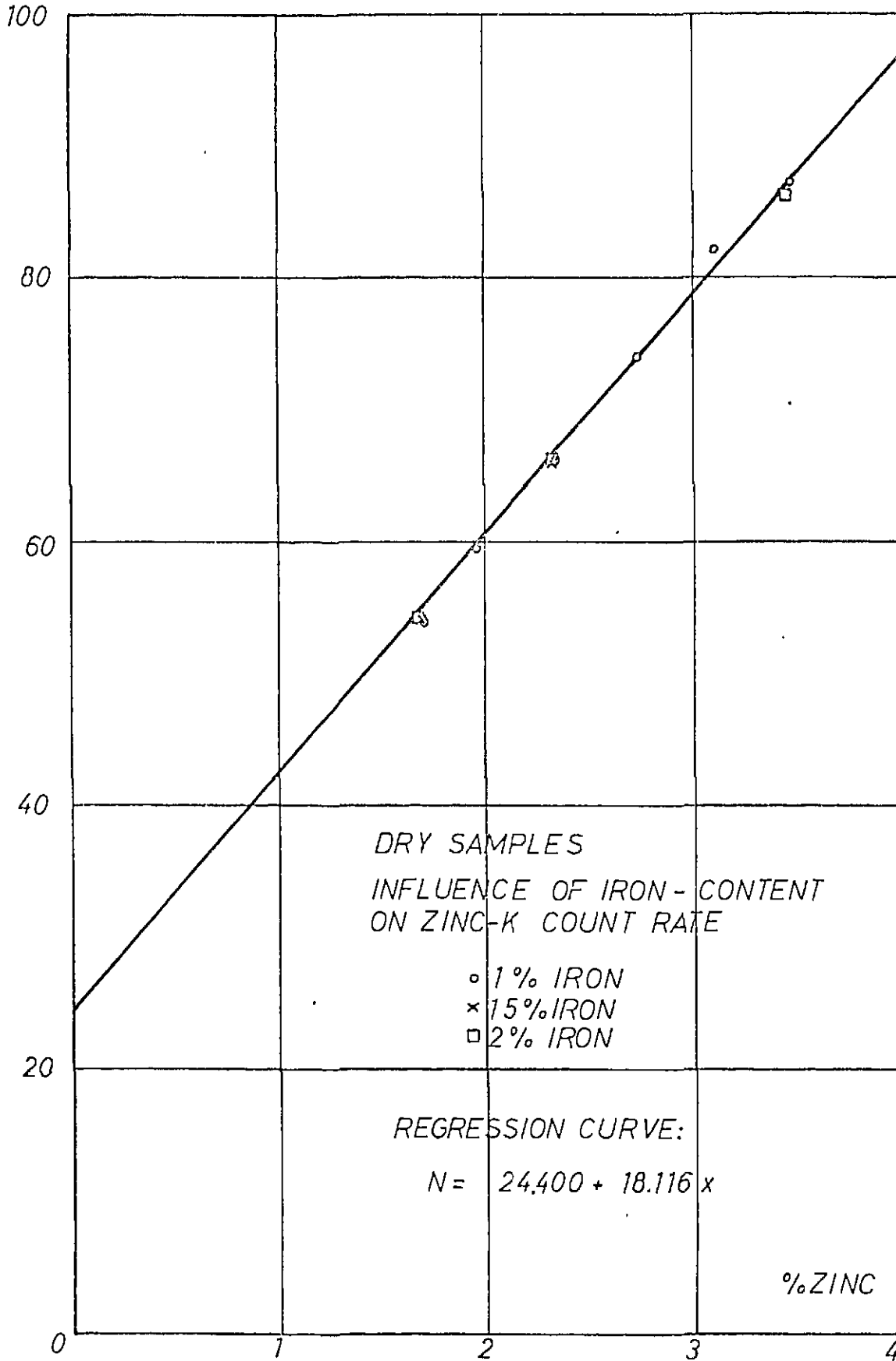


FIGURE 1

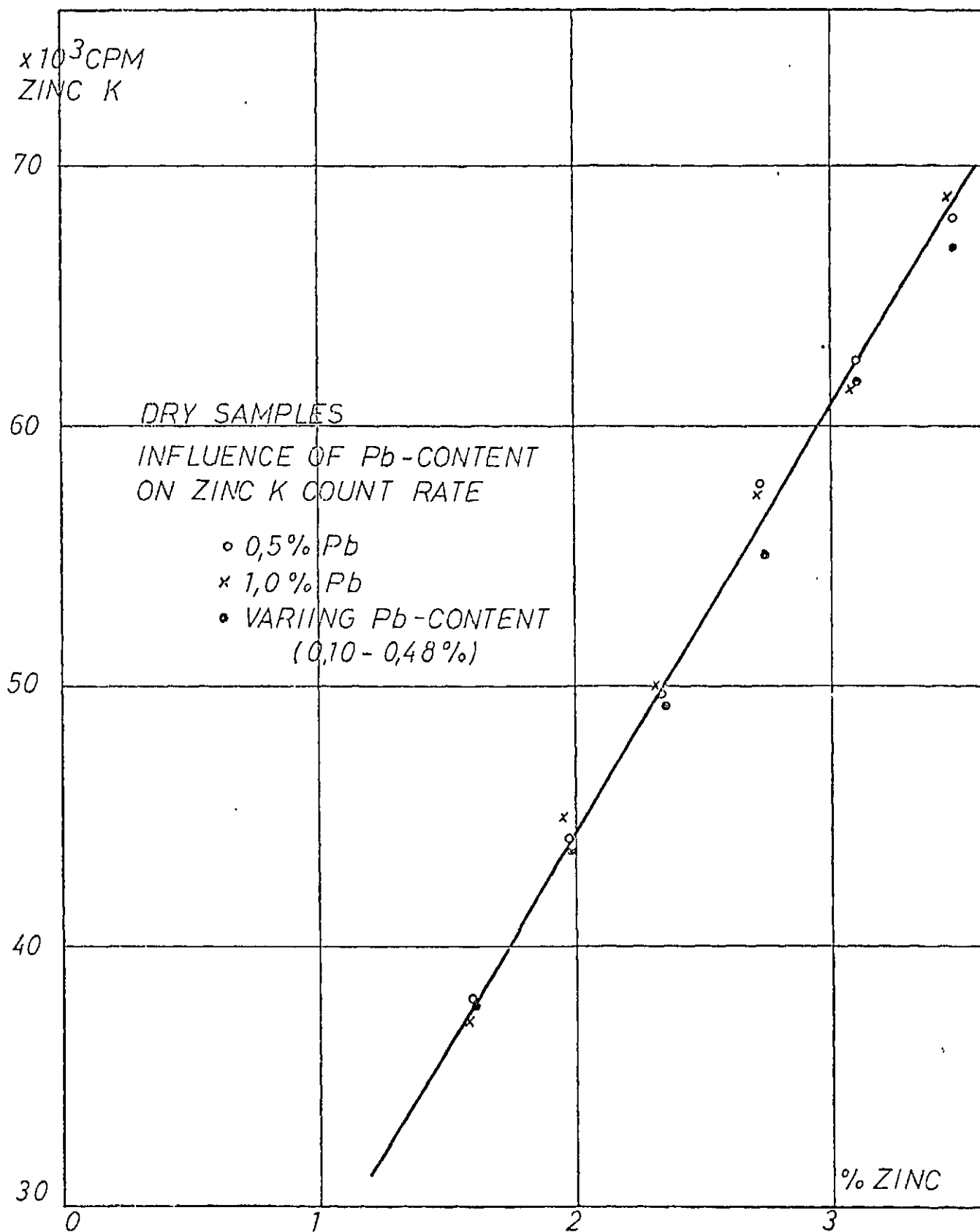
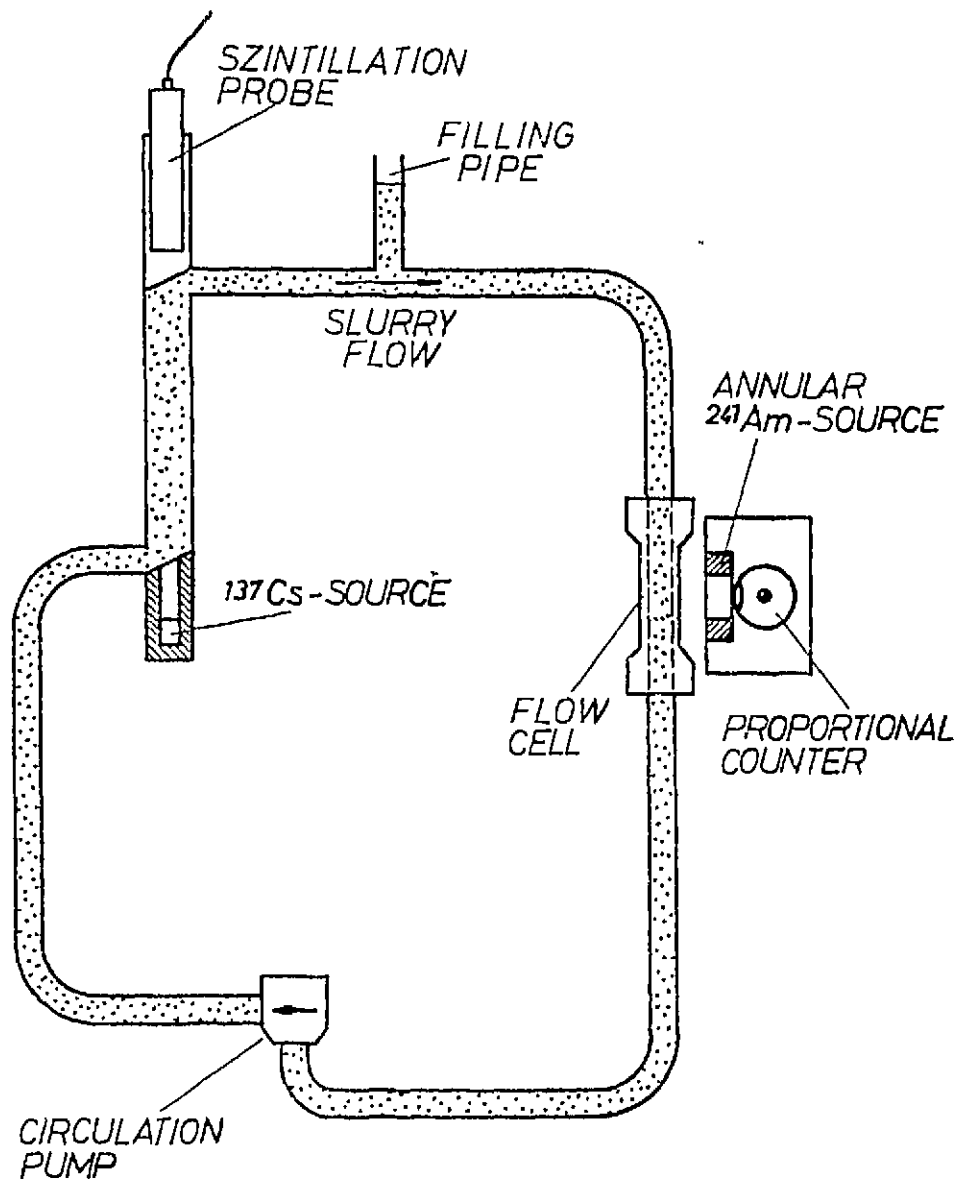
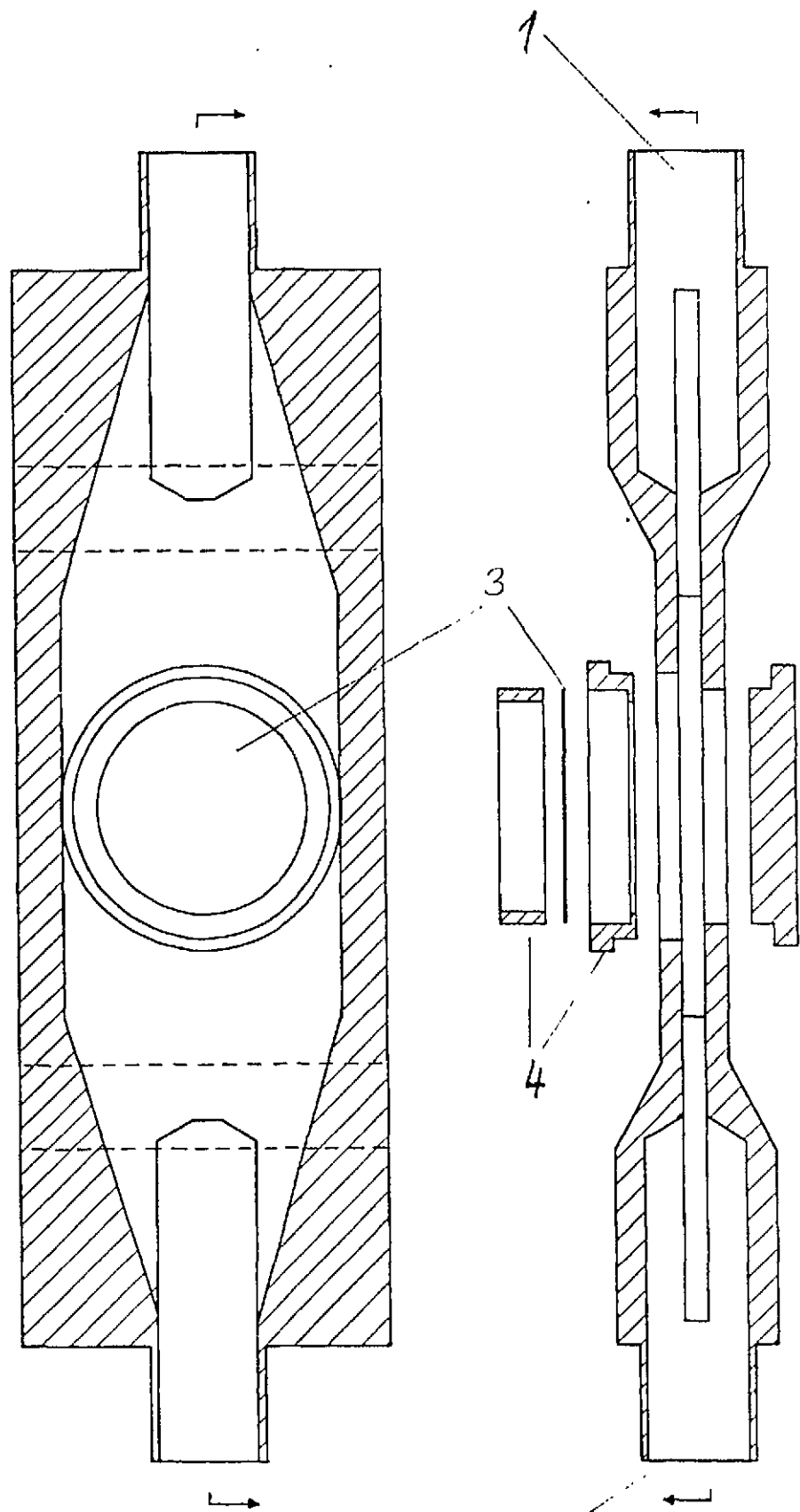


FIGURE 2



SCHEMATIC DIAGRAM OF SLURRY TEST LOOP

FIGURE 3



- 1 - SLURRY INLET
- 2 - SLURRY OUTLET
- 3 - BE-WINDOW
- 4 - WINDOW MOUNTIN AND SEAL

FIGURE 4

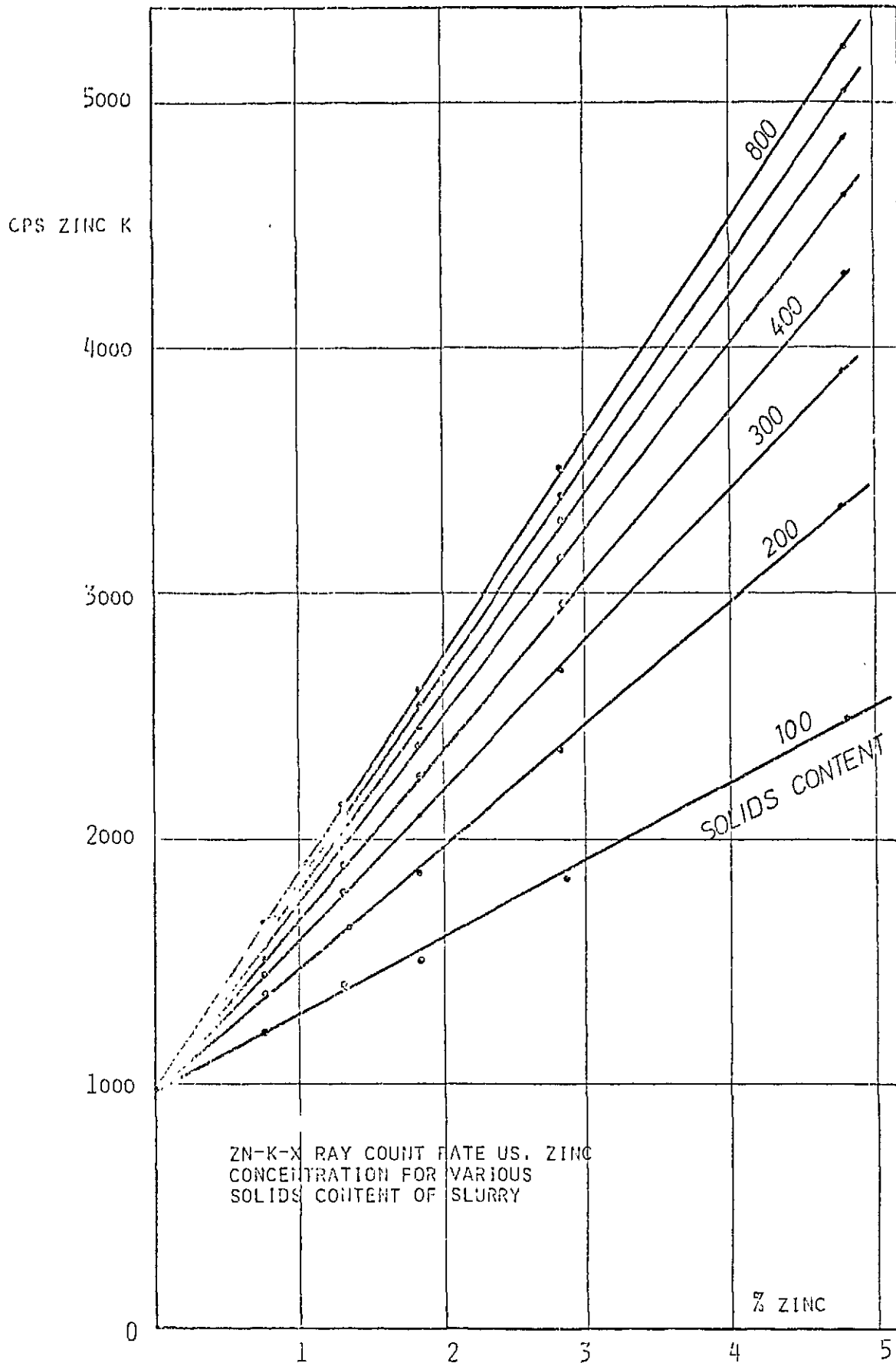


FIGURE 5

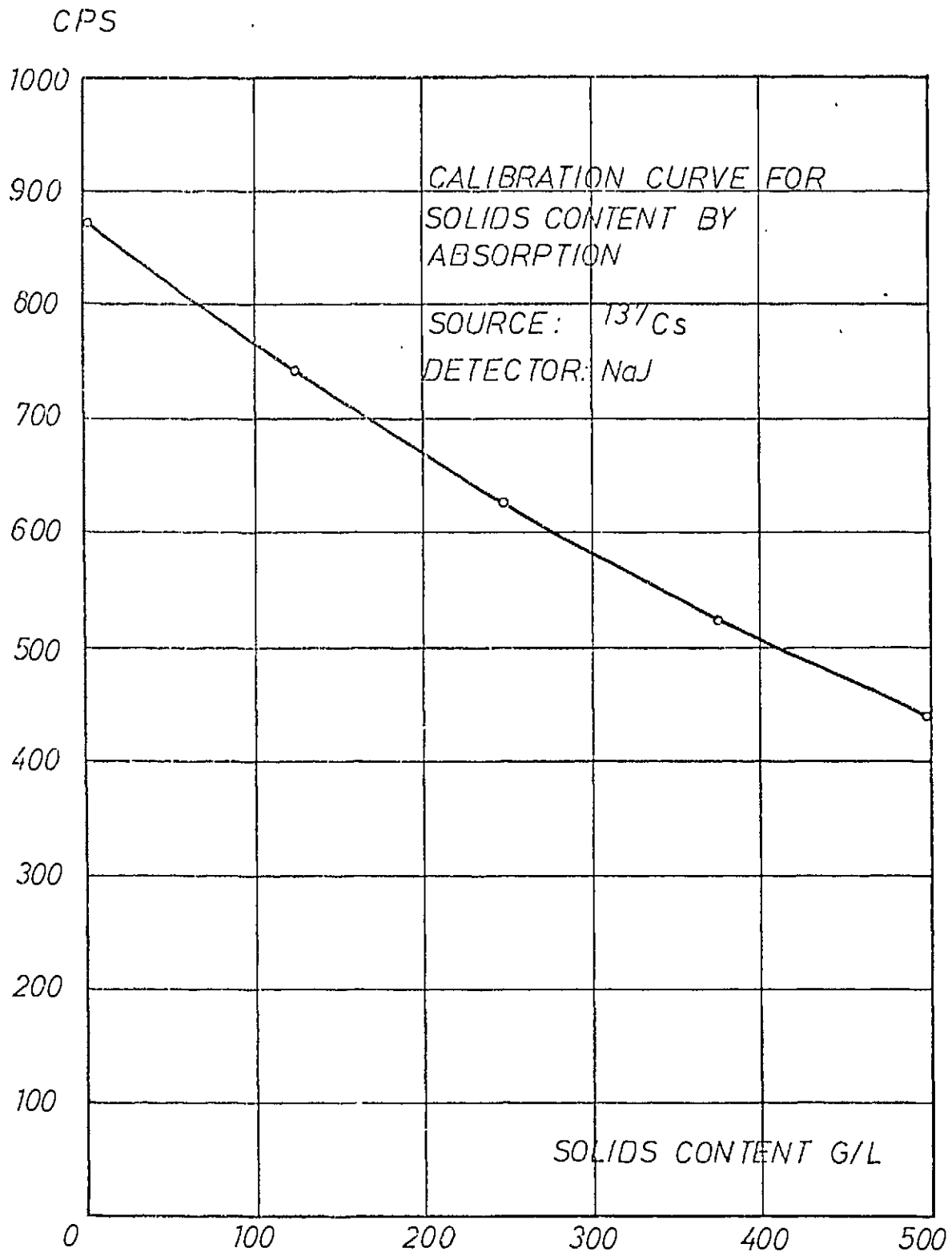


FIGURE 6

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