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NEW METHOD OF RAPID DETERMINATION OF K_2O IN FERTILIZERS

By

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In order to improve the supervision of the production of fertilizers by simplifying sampling and avoiding dissolving, we have considered the possibility of determining potash by measurement of the radioactivity due to potassium.

1. PRINCIPLE

1.1 The radioactivity of potassium.

The following is the isotopic composition of natural potassium:

^{39}K : 93.1%

^{40}K : 0.012%

^{41}K : 6.9%

The isotope ^{40}K is a natural radioelement with the following radioactive properties:

- Period : $1.3\,10^{9}$ years
- β emission : 1.32 MeV 89% disintegration
  K : 11% disintegration
- γ emission : 1.46 MeV 11% disintegration

One gramme of natural potassium is the centre of 120 disintegration per second. This very low radioactivity (about 10^{-3} μ Ci/g) is, however easily measured provided that a large sample is used. In the case of fertilizers this is an advantage; it would, in fact, seem to be easy to obtain a sample of 50 or 100 kilogrammes which is representative of the production in progress.

1.2 Principle of Measurement

Figure 1 represents the equipment used.

The γ photons are detected by means of a scintillator (monocrystal of sodium iodide activated by thallium) optically associated with a photomultiplier.

This unit transforms the γ photons into series of electrical pulses proportional in amplitude to the energy of the detected radiation. After amplification these pulses are analysed by an amplitude code which transmits them into one of the 200 channels of the magnetic store of the selector (as a function of the calibration of the amplifier).

These pulses are stored and visually displayed on an oscilloscope (Figure 2a Spectrum of Pure ^{40}K). The absciss of the top of the peak corresponds to the energy of the detected radiation; the area of this peak is proportional to the number of disintegrations which have occurred during the counting time and thus to the amount of radioelement present in the product under examination.

These results are given directly in digital form by output devices: electronic integrator and printer.

2. STUDY OF THE γ SPECTRUM OF FERTILIZERS

The ternary NPK or binary PK fertilizers are prepared by mixing or by causing chemical reactions between a natural phosphate, phosphoric acid, nitric acid, ammonia and potassium chloride. The resultant natural phosphates and therefore phosphoric acids contain traces of uranium (approximately from 50 to 300 ppm according to the source of the phosphates).

In the natural phosphates uranium is in equilibrium with its daughter elements (Figure 3); in phosphoric acid this balance is broken and the radioactive emission is bound to the age of the phosphoric acid (in fact some daughters of uranium have a rather short life and are re-formed). The release of radon 222 is caused in a random and incomplete manner at the time of the nitric attack of the phosphates.

The γ spectrum of a ternary fertilizer is thus rather complex (Figure 2C). One of the daughters of uranium ^{214}Bi emits γ photons of 1.38 MeV. The separative power of the detector is insufficient to differentiate these photons from the 1.46 MeV photons due to ^{40}K. A correction is therefore necessary.

Let us once again take the four spectra represented in Figure 2.

A - Pure potassium spectrum less background noise

B - Uranium spectrum (natural phosphate)

C - Spectrum of a ternary fertilizer

D - Spectrum obtained with sand (absence of U and K) giving the background noise.

The C spectrum is the sum of the A B D spectra in these conditions written as:

NT = NK + NU + NB (1) 1.46 MeV band

nT = nK + nU + nB (2) 0.61 MeV band

wherein:

K = concentration of potassium

U = concentration of uranium and daughters

B = background noise

For a given radioelement in given geometrical conditions, the relation between two different energy lines is constant, hence

$$\frac{NK}{nK} = CK \qquad (3)$$

and

$$\frac{NU}{nU} = jU \qquad (4)$$

by carrying forward in 1 and 2 we get

$$NK = \frac{NT}{\frac{1-jU}{CK}} - \frac{jU\ nT}{\frac{1-jU}{CK}} - \frac{NB}{\frac{1-jU}{CK}} + \frac{jU\ nB}{\frac{1-jU}{CK}} \qquad (5)$$

The terms NB and nB are constant for a given counting time, unless there is a considerable movement of potash in the vicinity of the probe. It is therefore important to avoid any accumulation or movement of potash near the measuring equipment.

The term jU is obtained by carrying out a measurement with phosphate alone.

The term CK is obtained by taking a measurement with potassium chloride.

Statistical error in measurement

Radioactive disintegration is a phenomenon which obeys the laws of chance.

In a measurement during which N pulses are counted, there will be a probability of 84% that the error ΔN will be such that

$$N - \Delta N \quad < N \text{ true} \quad < N + \Delta N$$

$$\text{if} \quad N = \sqrt{2\sigma} \quad \text{with } \sigma = \sqrt{N^2}$$

If we refer to relation (5) it will be seen that:

$$\sigma \text{ total} = \sqrt{{}^2NT + \sigma^2\ nT + \sigma^2\ NB + \sigma^2\ nB}$$

from which we obtain*

$$NK = \sqrt{2\ (NT + nT + nB + nB)}$$

It will be seen that for potash the accuracy of the measurement of activity will be made to within about 1% if we take into account at least 20,000 pulses due to ^{40}K.

3. EXPERIMENTAL TECHNIQUE

We have seen that in order to obtain a precision of 1% it was necessary to count at least 20,000 pulses due to ^{40}K. Taking into account the efficiency of the detector and the grade of the fertilizer and the first tests carried out, we are led to use a sample of at least 50 Kg of fertilizer. The pulses received by a 3" x 3" scintillator are counted for 15 minutes.

The first tests gave rise to some difficulties of reproducibility. Analysis of the results led to these difficulties being attributed to differences in the density of the fertilizers. In order to remedy this we have investigated the "infinite" geometric conditions, that is: the volume of fertilizer which must

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*This calculation leads to the most pessimistic estimate of the error.

surround the detector so that the measurement carried out may become independent of the mass of fertilizer; the only variable affecting the net count being the potash content.

A series of tests has made it possible to determine experimentally that the probe must be surrounded in all directions by at least 25 cm of fertilizer.

We have had the measuring cell modified so that the probe is in conditions of infinite geometry. Figure 4 shows a representation of this enclosure.

4. RESULTS

Having fixed the experimental parameters we proceeded with a calibration connecting the ^{40}K activity to the chemically determined potash content.

In order to make sure of good correction we have by a method of calculation (use of the EMD/8/48 machine) investigated the coefficients jU and CK by using a multiple linear regression involving 2 independent variables.

$$X_1 = A + B_2X_2 + B_3X_3$$

Under these conditions we obtain for the ternary fertilizers:

$$NK = -0.609 + 0.0423\ NT\ 10^{-2} - 0.106\ nT\ 10^{-3}$$

The results are given in the following table and in Figure 6.

23 - 6

P_2O_5	Nitrogen	nT	NT	K_2O chemistry	K_2O radio	deviation

23 - 8

Sample	NT	nT	K_2O chemistry	K_2O radio	R-C
K1	118 229	81 111	20,28	20,08	- 0,20
K2	91 158	62 042	15,35	15,36	+ 0,01
K3	90 976	61 209	15,42	15,37	- 0,05
K4	93 102	65 173	15,08	15,61	+ 0,53
K5	91 878	63 380	15,10	15,45	+ 0,35
K6	93 621	65 101	15,41	15,73	+ 0,32
K7	95 326	65 757	15,67	16,06	+ 0,39
K8	93 982	64 368	16,12	15,85	- 0,27
K9	94 706	63 772		16,03	
K10	97 901	64 901	16,10	16,55	+ 0,45
K11	94 913	65 005		16,01	
K12	95 581	65 817	15,90	16,11	+ 0,21
K13	94 453	64 979	15,75	15,91	+ 0,16
K14	98 052	65 787		16,66	
K15	98 365	65 752	16,23	16,80	+ 0,57
K16	96 706	64 623		16,45	
K17	92 813	64 557	15,22	15,59	+ 0,37
K18	99 226	68 184		16,75	
K19	94 502	66 321	15,47	15,85	+ 0,38
K20	96 191	65 922	15,61	16,23	+ 0,38
K21	97 124	63 454		16,56	
K22	97 407	63 918	15,90	16,61	+ 0,71
K23	97 793	67 641		16,47	
K24	101 603	68 751	16,91	17,32	+ 0,41
K25	99 486	68 949	16,48	16,76	+ 0,28

The deviation K_2O chemistry, K_2O radiometry on a single result is 2%. This difference is slightly greater than that provided for in theory, under the conditions of working at the limit of the possibilities of the methods employed. It should, however, be noted that the fertilizer used in this last test sometimes had a temperature of the order of 40 to 50°C, which involves slight deflections of the electronic devices (photo multiplier and preamplifier), but it is desirable to avoid such differences of temperature as far as possible.

Following these tests carried out in one of the factories of the group, a new programme was launched in another factory where the production proceeds on a slightly different principle. During this programme 146 samples were investigated. The correlation between the results given by the radiometric method and the chemical analysis performed by gravimetry of potassium tetraphenyl boride is excellent. Graph 7 shows the results.

5. CONCLUSION

It has been found possible to check the potash content of fertilizers by radiometry. When the manufacturing workshop is equipped with an automatic sampling chain it is possible, for example, to take 60 Kg of fertilizer per hour for a production of 30 tons per hour. Thus a large sample is used which is far more representative of the output than the sample for chemical analysis, and any division of the manufacturing sample is avoided.

The method has the following characteristics:

- mean difference with the TPBK method = $\leqslant$ 2% for a single sample
- response time: $\leqslant$ 30 minutes
- investment in electronic equipment: ≃ 50 000F.
- volume of fertilizer necessary for the measurement: ≃ 100 litres, ie 110 to 120 Kg

We should like to express our thanks to our colleagues, Messrs Depommier, Sogne and Labat for their very valuable assistance in this investigation.

We should also like to thank the Research Board and the Board of the Fertilizer Group who allowed us to carry out these tests.

DISCUSSION

(Slides were shown during Mr. Vérot's presentation)

MR.J.L.VEROT (Générale des Engrais,S.A.,France): In order to make it easier to check the potash content of fertilisers, by simplifying sampling and limiting the need to dissolve the product, we have investigated the possibility of determining the potash content of fertilisers by using the natural radioactivity of isotope 40 of potassium. This isotope is present in natural potassium in proportions of 0.012%, which results in the measurement of very low radioactivity, but in our case this is an advantage, since we use a very large sample of about 100 kilos. The first slide shows the principle of measurement and the apparatus. The fertiliser is contained in the vessel on the right in the diagram and we have found by experiment that the probe must be surrounded by at least 25 cm. of fertiliser. This probe, which consists of a crystal of sodium iodide activated by thallium, transforms the gamma photons into electrical pulses proportional in amplitude to the energy of these gamma photons. The electrical pulses are stored in the 200 channels of the memory in terms of their energy, as displayed on the oscilloscope. Each peak corresponds to a radio-element, and the area of the peak, i.e. the number of disintegrations recorded during the counting time, is proportional to the content of potassium 40, i.e. the potash content of the fertiliser.

Side 2 shows us a spectrum of potassium alone, with a spectrum of uranium below and the spectrum of a ternary fertiliser at bottom right. These ternary fertilisers contain traces of uranium brought in by the phosphate. Unfortunately, one of the daughters of uranium emits radiation which is located at precisely the same place as potassium 40 radiation. We are therefore obliged to make a correction similar to that made when using the colorimetry process on the basis of two wavelengths, and from the number of pulses counted in the measurement band we take a certain number determined by the ratio of NU to nU, which enables us to determine the interference caused by the presence of uranium. To gauge our technique (slide 3), we used known fertilisers with a potash content determined by the gravity method using potassium tetraphenylborate. We find that the correlation between the content as determined by radiometry and the content determined chemically is excellent.

On the basis of this standardisation, we carried out a measurement study in one of the plants in the Group (slide 4). During this operation, we analysed 164 samples and found that the correlation between the potash content determined by radiometry and the potash content determined chemically was excellent, with the exception of a few points marked with a cross where the deviation was too great. At the moment, we are unable to explain these deviations satisfactorily.

In conclusion, we can confirm that it is possible to check the potash content of fertilisers by radiometry. The manufacturing plant must be equipped with an automatic sampling system which will allow 60 - 100 kilos of samples to be taken from a production of 30 tons/hour. The measurement can thus be carried out on a much larger sample than in the case of chemical analysis, and there is no need to divide it up or to dissolve it. The characteristics of the method are as follows: the mean deviation in respect of gravity determination using potassium tetraphenylborate is less than 2% for an isolated sample. The response time is less than 30 minutes, averaging 15 to 20 minutes. Investment in electronic equipment is in the region of 50,000 French francs, and the quantity of fertiliser needed for each measurement, i.e. the sample, is of the order of 100 l., i.e. between 110 and 120 kgs. It is, however, possible to operate on 50 to 60 kgs.

MR. T. VAHERVUORI (Kemira Oy, Finland): May I thank you on behalf of the whole audience for your most interesting paper, and congratulate you on your valuable work.

The methods of fertiliser analysis have been developing constantly, but a new stage in the development of analytical methods for potassium has now been presented to us. This method meets the following requirements: the determination of potassium can be made from samples which are large enough to obviate the possible effects of a lack of homogeneity in the sample. Determination being relatively quick, checking can obviously be repeated quite often. These are definite advantages for which the authors are to be congratulated. I would like to ask Mr. Verot to comment on the following questions about practical work:

1) In your paper you mention the effect of temperature on the functioning of electronic devices. What, in your opinion, is the broadest acceptable temperature range? In practice this will probably mean that the sample cannot be analysed immediately after being taken from the process but that the various samples must be cooled to equal temperatures.

2) Will the handling of a sample which is as big as this cause dust problems? We have found that fluorine compounds contained in fertiliser dust are harmful to electronic devices.

3) Do you have any experience of the effects of vibration on electronic devices if they are placed in a manufacturing plant?

You have compared your method of analysis to the TPBK-method. We use a so-called auto-analyser for routine analyses. The margin of error in your method compared to the TPBK-method is lower than 2%, whilst ours is lower than 0.5%.

For the handling of single samples your method is quicker. For work in series our method is likely to be quicker. The preparation of a batch of samples takes 40 min. Once the processing of the liquids has started the speed is normally approx. 30 analyses/h. This figure includes approx. 12 standard liquids and 18 single tests, or the analyses of 9 double samples. Furthermore, we obtain determinations of NH_3 - and NO_3 - nitrogen simultaneously.

In practice your method is cheaper than ours, as the equipment is less expensive and there are no reagent costs.

Some further questions about your paper if I may:

4) In section 2, page 4, you mention that "The term jU is obtained by carrying out a measurement with phosphate alone." And earlier (p.2) "In the natural phosphates uranium is in equilibrium with its daughter elements; in phosphoric acide this balance is broken and the radioactive emission is bound to the age of the phosphoric acid." Does this mean that, when standardisation

is carried out by means of phosphate, the change of balance in phosphoric acid or the phosphate formed in the process from phosphoric acid must be considered when calculating the result, and how should this be done? Furthermore, does the age of the phosphoric acid have to be taken into consideration?

5) In what way is the background noise caused by uranium to be taken into account, if the quality of the phosphate rock used at the plant varies, and what happens if you pump acid produced from different phosphate rocks into the same phosphoric acid tank, before it is used for the production of fertilisers?

6) Our Uusikaupunki Works produces fertilisers based on wet process phosphoric acid and nitric acid in parallel. For the production of certain qualities different amounts of phosphoric acid are mixed into the nitric acid-raw phosphate slurry. On page 2, section 2, you mention that "The release of radon 222 is caused in a random and incomplete manner at the time of the nitric attack of the phosphates." Does this mean that the various production methods of fertilisers or the combinations of various production methods have to be taken into account in measurements?

It has been an honour to be allowed to comment on your paper, and I hope the audience will be as interested in your answers as I am.

MR. VEROT: It is very easy to answer the first question on the effect of temperature. Detectors are now available which operate very satisfactorily between -10 and + 60°C, which therefore makes it possible to test the fertiliser sample as soon as it leaves the unit, since it is at a temperature in the range 30 to 50-55°. With these new detectors, the problem of temperature no longer arises. Of course when the sample is handled, there is a lot of dust, but the electronic measuring equipment, (i.e. the electronic unit, the selector, visual display and output device which you saw on the first slide,) is connected to the probe by a 40 metre cable and the electronic apparatus is located in the control cabin in a closed unit of the glove box type, which fully protects it from dust.

Vibration is prevented by placing the box containing the electronic apparatus on anti-vibration pads. Now we come to the problem of comparison between the different methods of analysis: the auto-analyser has certainly a much faster output once the samples are prepared, and I consider that the two techniques are not competitive but strictly complementary. The advantage of radiometric measurement is that it provides for analysis of production approximately every 20 minutes, so that progress can be followed as it goes along, particularly in the case of a change of formula or if some malfunction is suspected in the plant. It is a very great advantage to have a much faster check on a specific part of the output of the plant. As to costs, they are comparable - there is the advantage of not having to use reagents. It is really a question of the internal policy of each manufacturer.

I propose to take your last questions together. The radio-element responsible for interference is not uranium itself but one of its daughters, bismuth 214. This bismuth 214 is derived from uranium via thorium 234, radon 226, radon 222. Radon 222 is a gas given off at random but there are two specific rays at 610 KeV and 1380 KeV (which is the one which interferes with potassium 40 at 1.46MeV.) The relationship between these two rays, under given conditions of measurement is a nuclear and physical constant. Whatever the content in radon and consequently in bismuth 214, the relationship between the 610KeV and the 1.38 MeV ray is constant. Thus the correction we apply is valid whatever the age of the phosphate, the radon content or the effect of the different random variables which may affect this quantity.

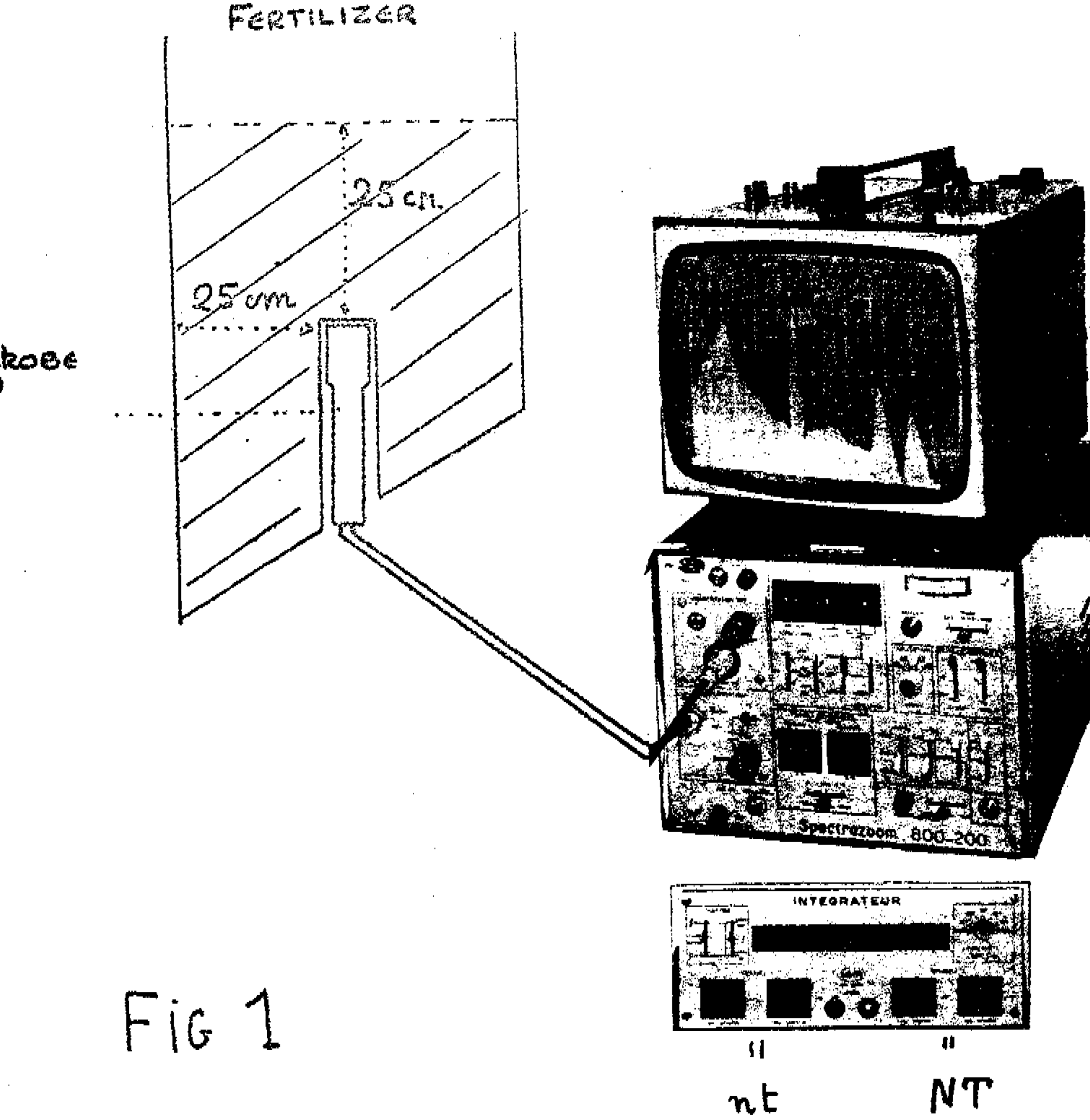
FERTILIZER
25 cm.
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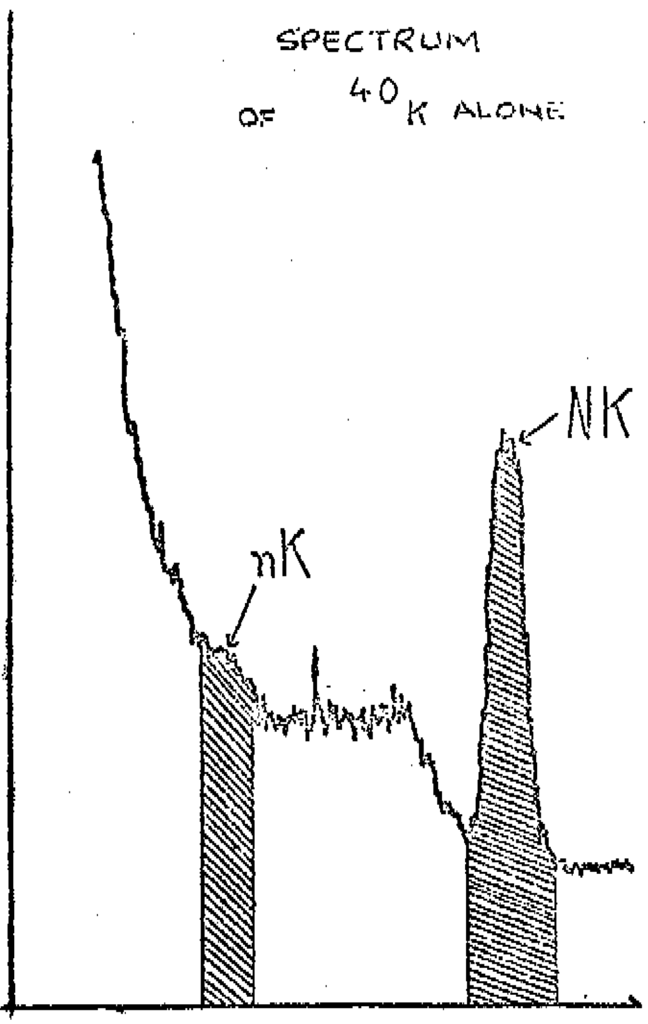
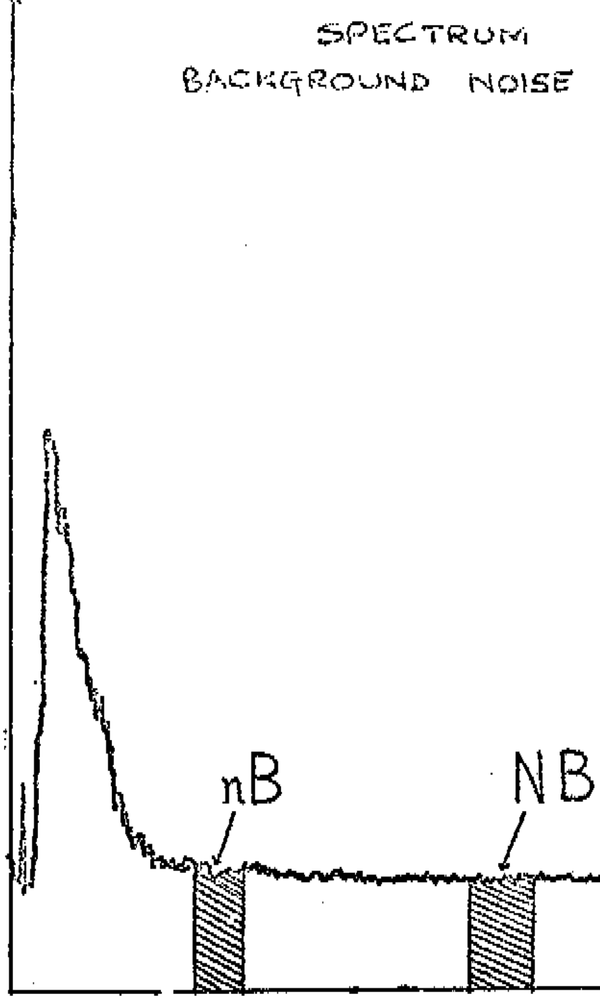
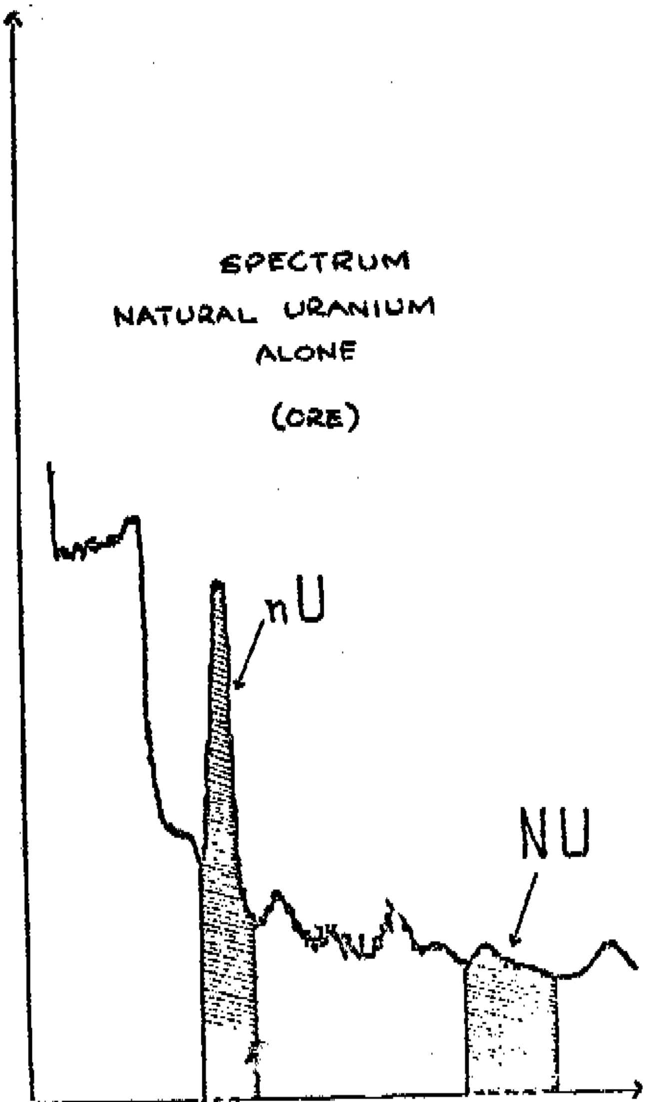
Fig 1



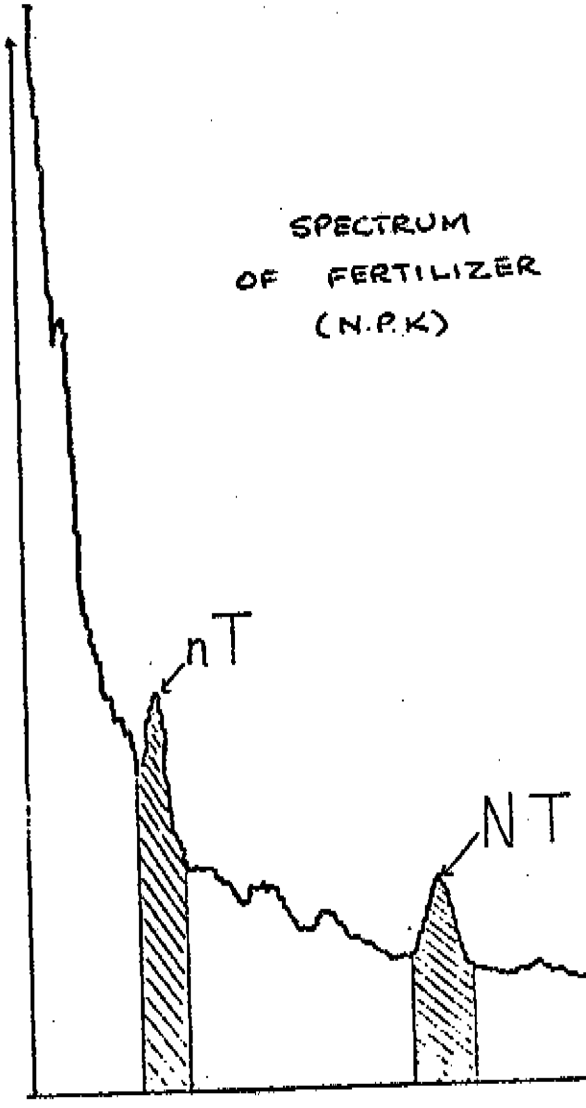
SPECTRUM OF ^{40}K ALONE



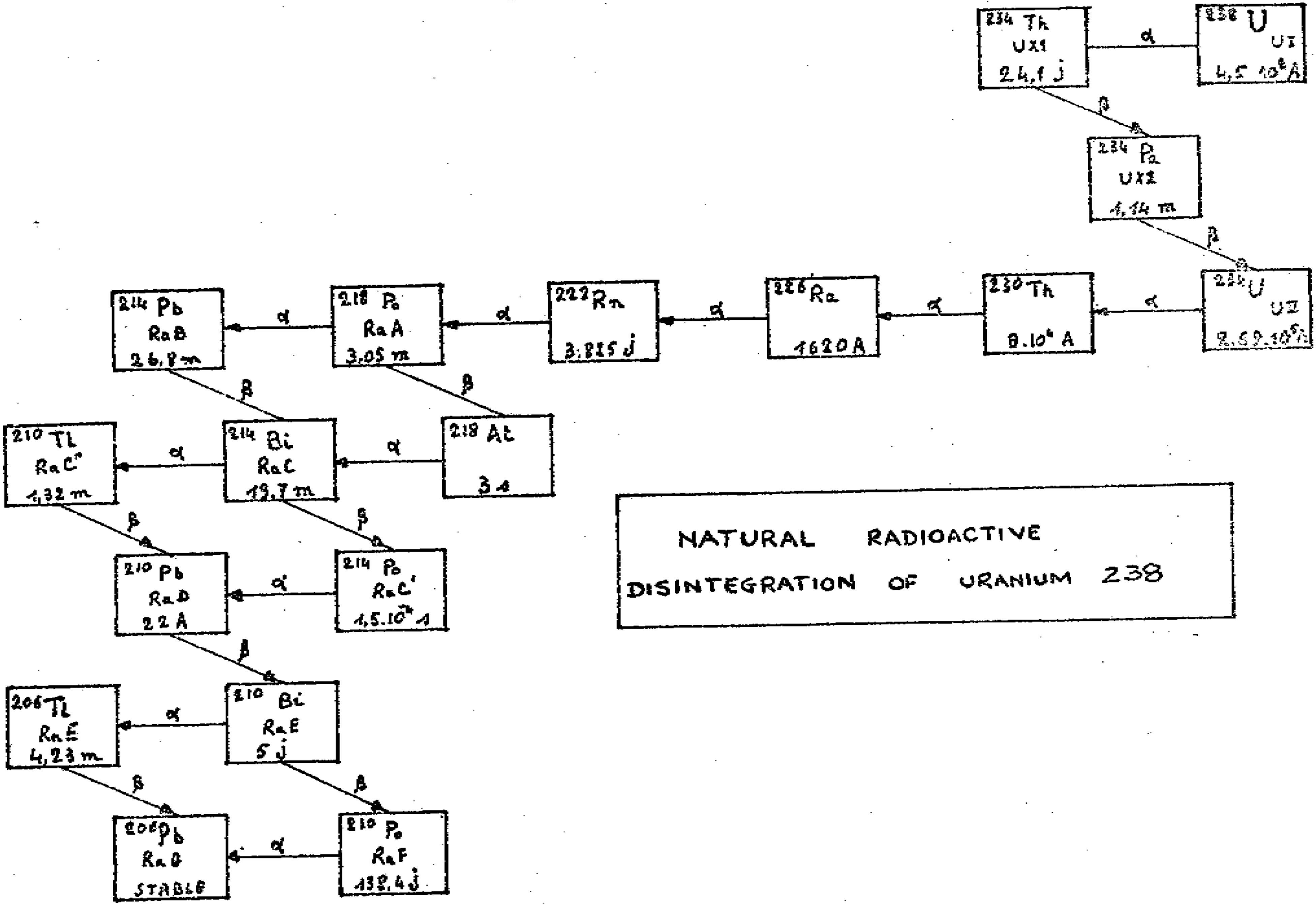
SPECTRUM BACKGROUND NOISE



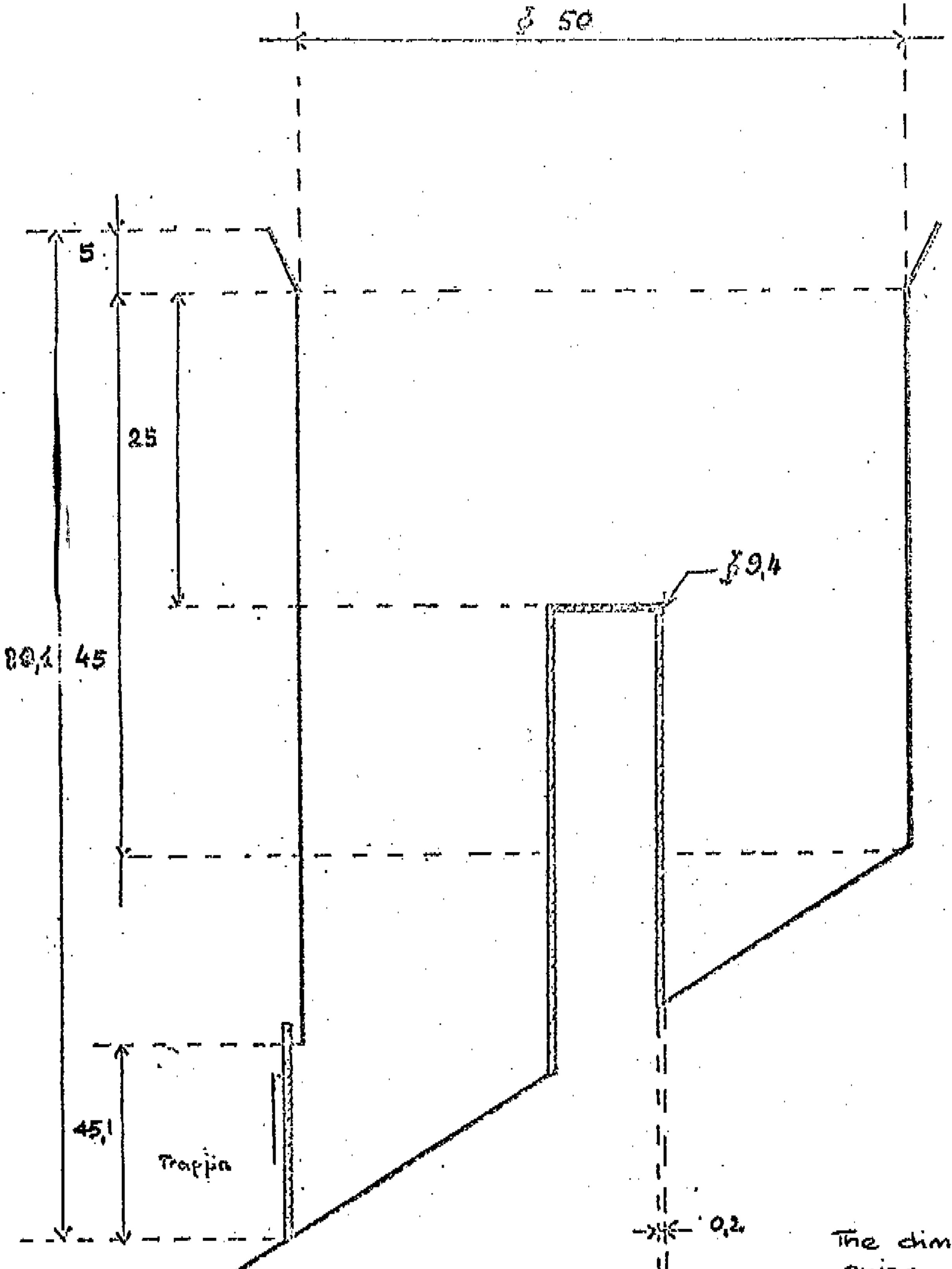
SPECTRUM NATURAL URANIUM ALONE (ORE)



SPECTRUM OF FERTILIZER (N.P.K)



NATURAL RADIOACTIVE DISINTEGRATION OF URANIUM 238



The dimensions a
given in cm.

Fig 4

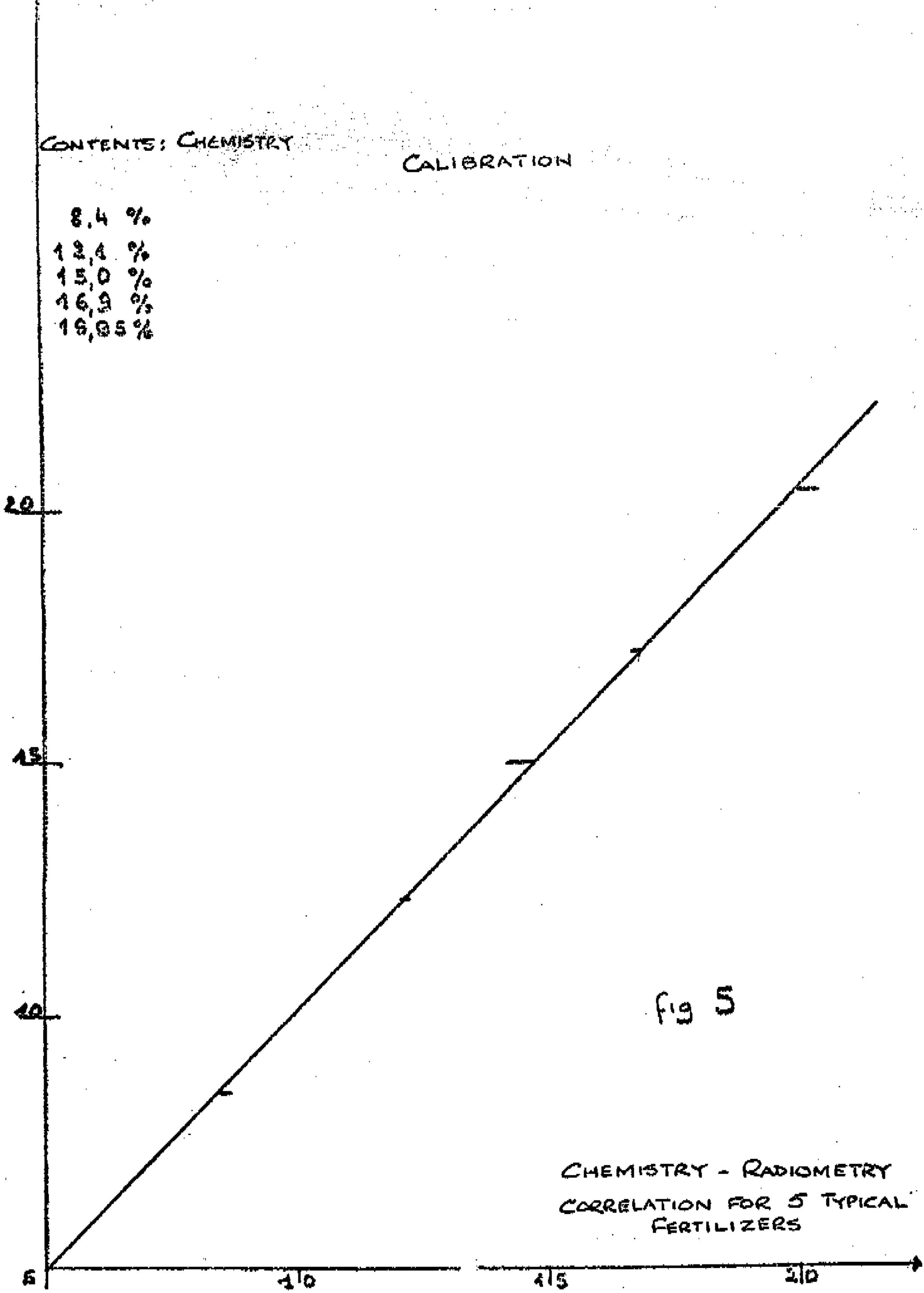


fig 5

CHEMISTRY - RADIOMETRY CORRELATION FOR 5 TYPICAL FERTILIZERS

CHEMISTRY - RADIOMETRY CORRELATION

Fig 6