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THE USE OF PHYSICAL METHODS FOR STUDYING AND
ANALYSING PHOSPHATIC FERTILISERS

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For several years research workers have been examining phosphate rocks and phosphatic fertilisers by physical methods and many works have appeared on this subject in the literature.   At the technical meetings of the I.S.M.A. held in September 1955, Dr. Berndt Meppen put forward in his paper on the theory of superphosphate attack some results which had been obtained by examining X-ray diffraction spectra and the discussion which followed proved that the I.S.M.A. was very interested in this research.   In the course of this work, we should like to describe certain outstanding aspects of the experiments carried out in our laboratory.

Our aim was to identify and to determine quantitatively some of the constituents of phosphate rocks and of fertilisers

- quartz and fluorine in phosphate rocks
- crystalline form of calcium sulphate in superphosphate or ammonia-
        ted superphosphates.
- the nature of the anion combined with the potassium in potassium
        fertilisers
- the quantity, by infra-red spectography, of the insecticides added
        to the fertilisers.

MATERIALS USED.

We were able to carry out the X-ray diffraction work by using a Philips Norelco apparatus which is made up of :

- a generator with an interchangeable sealed tube
- a goniometer with a Geiger Muller tube measuring the diffraction
        spectrum between -25° and 135°.
- a system of integrator calculation and of registering the
        intensity received on the Geiger Muller counter.

With this type of apparatus it was possible in most cases to determine with great precision the crystalline bodies whose concentration in the sample was higher than 0.5%.   For all our quantitative determinations we used the well-known method of internal standard, described very precisely by Alexander and Klug (X-ray diffraction procedure for polycristalline and amorphous materials - New York 1954).   This method can be summarised as follows:

When a crystalline compound, the internal standard, is added to the
sample to be analysed in a constant proportion x the concentration of
the element A to be determined is a linear function of the value of
the relation

1A - 1A intensity of a band typical of the element A
1s - 1s intensity of a band typical of the diffraction of the
                    internal standard.

We chose, of course, an internal standard which is chemically inert
and whose diffraction bands do not interfere with the bands of the
crystal being examined.

In infra-red absorption spectroscopy we use the well-known Perkin
Elmer spectrograph, model 12 C, with simple rays, and model 21 with
double rays, which allows, either with a prism of LiF or with a prism
of NaCl, ideal working with absorption in the region between 2 and
15 microns.   The application of Beer's law, relating the concentra-
tion to the optical density, enables us to carry out easily quantita-
tive estimations even in the case where several constituents are
mixed.

I - EXAMINATION OF PHOSPHATE ROCKS BY X-RAY DIFFRACTION.

The spectra for apatites are well-known;   amongst others we can
quote the work of McConnel in 1938 (Amer. Min. 23, 119) which gives a
detailed summary of X-ray diffraction spectra of phosphate rocks.
These spectra are very little different one from the other and it is
very often difficult to determine the form in which a phosphate rock
is found.   We have limited ourselves to research on and determination
of two minor constituents which are, nevertheless, important in the
course of the reaction of attack.

Determination of quartz.

The determination of quartz was carried out by adding to the
phosphate rock 10% of rutile as an internal standard.   After careful
grinding in a mechanical pulveriser to ensure homogeneity, we recorded
the spectrum so as to show the 3.24 Angström band of rutile and the
3.35 Angström band of quartz.   We compared the intensity of these
two bands with those of the mixed standards of pure tricalcium
phosphate, quartz and rutile.   We found the following results in
several phosphate rocks (we call to mind the percentage of SiO_2
found by usual chemical methods.)

Phosphate	Total SiO_2	Quartz
Morocco 79 - 80% B.P.L.	1.37%	0.8%
Morocco 75% "	2.32%	0.9%
Morocco 70% "	2.80%	1.5%
Gafsa 63-65% "	5.40%	0.6%
M' Dilla 65% "	4.10%	0.8%
Land Pebble	6.40%	4.2%
Kola	3.03%	0.4%

These results have already been presented to the I.S.M.A. (see
paper by H. Deloménie I.S.M.A. Sept. '55) in his paper on fluorine
solubilised during the attack of superphosphate;   they show that
silica in the form of silicate is more easily attacked by the combined
action of sulphuric and hydrofluoric acids and plays the most impor-
tant part in the liberationand solubilisation of the fluorine.

Determination of fluorine.

We have tried to carry out research on fluorine in the form of
calcium fluoride which is not combined in the formula of apatite.
From the chemical determination of P_2O_5 and of total fluorine, it

can be seen that the molecular ratio CaF_2 and $Ca_3(PO_4)_2$ does not correspond to the theoretical formula of apatite - $CaF_2 [-Ca_3(PO_4)_3]3$

Phosphate	Molecule of CaF_2 per mol. of $Ca_3(PO_4)_2$
Theoretical Apatite	0.333 molecule
Morocco 79 - 80% B.P.L.	0.402 "
Morocco 75% "	0.437 "
Morocco 70% "	0.446 "
Gafsa 63 - 65% "	0.432 "
M' Dilla 65% "	0.441 "
Land Pebble	0.420 "
Kola	0.298 "

Except for Kola, the molecular ratio is clearly higher than that in apatite. Two hypotheses are possible. Either the calcium fluoride is in a solid solution in the apatite, or there is some free calcium fluoride in the gangue. The examination of the preceding table tends to confirm the second hypothesis; the richer the Moroccan phosphate, the smaller the value of the molecular ratio of calcium fluoride, a certain percentage being eliminated with the gangue.

In our X-ray diffraction spectra we identified and determined the free calcium fluoride, paying attention to the fact that certain bands of calcium fluoride interfered with the phosphate bands. We found the following values:

Phosphate	CaF_2 %
Morocco 79 - 80% B.P.L.	1.3%
Morocco 75% "	1.85%
Morocco 70% "	1.85%
Gafsa 63-65% "	0.9%
M' Dilla 65 % "	1.2%
Land Pebble	1.7%
Kola	invisible

If we calculate the new molecular ratio between CaF_2 and $Ca_3(PO_4)_2$ after having subtracted the percentage of free calcium fluoride found by X-ray diffraction, we get:

Phosphate	Molecule of CaF_2 per mol. of $Ca_3(PO_4)_2$
Theoretical apatite	0.333
Morocco 79 - 80% B.P.L.	0.335
Morocco 75% "	0.340
Morocco 70% "	0.341
Gafsa 63 - 65% "	0.375
M' Dilla 65% "	0.367
Land Pebble	0.330
Kola	0.298

The values are much closer to the theoretical molecular ratio of the apatite, in particular for Moroccan phosphates and for Land Pebble phosphate. The calcium fluoride, therefore, is certainly part of the gangue.

We would also point out that the close relation found for Moroccan phosphates is a good example of correlation giving an idea of the precision which we attained in our determinations by X-ray diffraction.

II – CALCIUM SULPHATE.

Calcium sulphate is one of the usual constituents in a large number of phosphatic fertilisers and consequently authors who have studied superphosphate by X-ray spectrography have identified the diffraction rays of calcium sulphate in their spectra. At the last I.S.M.A. Technical Meetings in September 1955, Dr. BERNDT MEPPEN in his outstanding paper on the theory of superphosphate attack linked the former theories with recent discoveries. PY. KRAINII and AA. MATWEENKO (Nauch. Zapiski Odessk. Politeh. Inst. 1954, 2, 265-70) give identical conclusions. Briefly, calcium sulphate is present in superphosphate almost solely in the form of anhydrite and in small quantities in the form of hemi-hydrate. Nevertheless, it is possible to see in the X-ray diffraction spectrum of a superphosphate rays which could be attributed to $CaH PO_4 - 2 H_2O$ which is isomorphou to gypsum and to dicalcium phosphate.

In interpreting our spectra, we have, in fact, found these re-sults. We wanted to make a quantitive determination of anhydrite hemi-hydrate in an 18% superphosphate (which had been stored for four months) where we had found by chemical analysis 31.4% total SO_3. By difference, we would thus have the percentage of gypsum without, however, knowing for certain whether there was a double crystal with the dicalcium phosphate, the bands of diffraction being identical.

We used rutile as an internal standard. The bands of rutile did not interfere with those of the constituents of superphosphate. By measuring the relations of the rays of rutile-hemihydrate and rutile-anhydrite and comparing them with the relation of the intensity of standard mixtures, we found the following results:

anhydrite   43% or 25.3% of SO_3
hemihydrate   6% or 3.4% of SO_3

There is therefore a deficiency of 2.7% in the total balance of SO_3, a difference which is much higher than the errors in the chemi-cal analysis of SO_3 and in the analyses by X-ray diffraction of anhydrite and hemihydrate. There is, therefore, a certain quantity of SO_3 in the form of gypsum or in the form of a crystal mixed with dicalcium phosphate if we take it for granted that all the iron is in the form of iron phosphate.

In the case of neutralised fertilisers, it is interesting to carry out research on calcium sulphate.

When we have an ammoniated superphosphate obtained by the reaction of a phosphate rock withssulphuric acid in the presence of sulphate of ammonia - for example with an ammoniated superphosphate with the following composition:

|	
Water-soluble ammoniacal N	5.26%
Total ammoniacal N	5.34%
Free P_2O_5	1.77%
Water-soluble P_2O_5	13.74%
Water- and citrate soluble P_2O_5	13.98%
Total P_2O_5	15.62%
Insoluble P_2O_5	1.64%

We were never able to reveal in our X-ray diffraction spectra the typical bands of sulphate of ammonia corresponding to the excess of SO_3. Next to the bands of anhydrite and of monocalcium phosphate

are found the bands of $(NH_4)_2 SO_4 - CaSO_4 - H_2O$. We may presume, therefore, that in this reaction the mixture of sulphuric acid and sulphate of ammonia react on the phosphate rock, giving ammonium phosphate or ammonium-calcium phosphate which makes the water-soluble P_2O_5, the excess sulphate of ammonia forming crystals with the calcium sulphate present and giving the $(NH_4)_2 SO_4 - CaSO_4 - H_2O$ crystal of the syngenite type.

On the other hand we have also examined a nitrogenous fertiliser obtained from mixing 18% superphosphate and sulphate of ammonia. In the X-ray diffraction spectrum of the fertiliser we again found the bands of sulphate of ammonia which had not been able to form crystals with the calcium sulphate already existing in the superphosphate. We would point out, however, that by adding water and by grinding the fertiliser, bands due to sulphate of ammonia disappeared gradually and syngenite was formed.

III. POTASSIUM IN FERTILISERS.

In our study of fertilisers we noticed the facility with which potassium has been added to the fertiliser in the form of potassium chloride quickly become combined with another anion. The most simple instance which served as a point of departure is outside the programme of the I.S.M.A., but it enables us to explain more easily the case of ternary fertilisers. It is concerned with a mixture of ammonium nitrate and potassium chloride. It is possible to note that a simple dry grinding of the two constituents gives rise to part of the reaction;

$$NH_4 NO_3 + KCl \longrightarrow K NO_3 + HN_4Cl$$
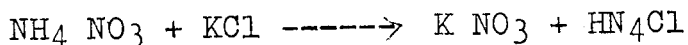
when a few per cent of water is added the reaction is completed in a few minutes. In order to make a quantitative determination of the rate of the reaction we were not able to use the method of internal standard which necessitates grinding. We should have had an irreversible condition of the reaction. Neither could we mix K Cl and NH_4 Cl where the reaction is impossible for the two crystals mix badly and form solid solutions (Perman and Sanders, J. Chem. Soc. 1923, 123, p 841, Jänecke, Z. Agnew. Chem. T.41, 1928, p 916).

We solved this problem by making initially curves showing the variation of the intensity of the bands of each of the constituents with an inert compound whose bands do not coincide with those of chlorides or nitrates. We chose in this case anatase which was well crystallised and had no chemical activity in our reaction. We traced the experimental curves:

$$I(K Cl) = f_1(I(TiO_2)) \qquad I(NH_4 Cl) = f_2(I(TiO_2)) \text{ etc...}$$

thus we were able to deduce theoretical curves, valid in our measuring conditions (apparatus, anticathode, aperture angle of the Bragg system)

$$I(K Cl) = F(I(NH_4 Cl)) \dots$$

In order to examine a fertiliser, we avoided as much as possible grinding or we only ground it very coarsely. We eliminated errors of homogeneity by examination of a small sample, and calculating the average intensity for 5 or 6 recordings, each made on a separate sample. The formation of 1.0.0 of the potassium chloride crystal having an important reflecting power, we were able to reveal and analyse easily by X-ray diffraction percentages of K Cl higher than 0.2%. The sensitiveness of this measuring method will be sufficient to enable the amount of reaction to be valued.

In ternary fertilisers with which we are concerned here, we can consider several cases according to the method of manufacture.

Among the compound fertilisers, one of our fertilisers has the formula 5.9.10, containing ammoniacal nitrogen and potassium; the progress of the reaction is exothermic and contains a liquid phase, and so we no longer find   in the fertiliser potassium in the form of potassium, chloride but in the form of potassium sulphate and syngenite $CaSO_4 - K_2SO_4 - H_2O$. The ammonia occurs in the form of ammonium chloride, ammonium phosphate and ammonium-calcium phosphate. We note here a series of reactions which are exactly similar to those of nitrogeneous fertilisers which we described earlier.

In a mixed fertiliser where potassium chloride is added to a fertiliser which has already been made, the reaction only occurs during the grinding, especially if a little water is added. In all our experiments, the fertilisers, which were in a granulated form which entailed grinding after adding water, are always reacted; potassium occurs in the form of potassium sulphate and the nitrogen partially in the form of ammonium chloride. In fertilisers sold in powdered form 50 to 70% of the potassium remains in the initial form of potassium chloride.

There exist, finally, fertilisers containing nitric nitrogen and ammoniated nitrogen; these fertilisers are obtained by the reaction of phosphate rock with nitric acid, and we observed the same categories as we have just described. In compound fertilisers or granulated fertilisers potassium occurs in the form of potassium nitrate; in this case we can determine the nitrate and the chloride by the internal standard method, the reaction being complete.

In a 14.12.16 fertiliser we should have in theory after chemical analysis:

34.4% of KNO_3
11.3% of NH_4NO_3
25.3% of NH_4Cl
0%   of KCl

we found by X-ray diffraction the following:

33% of KNO_3
25% of NH_4Cl
       K Cl was invisible.

These results compare very well and, except for errors in analysis, we can assert that all the potassium is in the form of potassium nitrate.

In mixed fertilisers we will have the mixture of ammonium nitrate, potassium nitrate, ammonium chloride and potassium chloride, the rate of the reaction varying within extremely large limits.

IV DETERMINATION OF ORGANIC PRODUCTS IN FERTILISERS.

Methods of analysis by spectrography using infra-red absorbtion have enjoyed very important developments after 1945, when industrialists were able to obtain on the market accurate apparatus with relatively simple controls. Nowadays, this method of analysis has risen among the most up-to-date methods especially in organic chemistry where it is often indispensable for determining the exact percentage of a particularly interesting isomer.

We must not, however, ignore the fact that the use of an Infra-Red spectography is not universal and, especially, that it is necessary to work in good conditions of dispersion in the longitudinal region of the wave in order to avoid systematic errors.

In the present case when examing fertilisers we find more and more on the market fertilisers mixed with organic products in order to combine fertilising action with an insecticide treatment. At present superphosphates or compound fertilisers are being sold to which hexachlorocyclohexane, aldrin, dieldrin, chlordane etc have been added, if we mention but a few of the most recent.

For the manufacturer it is most necessary to know the exact quality of the mixture, the content of the insecticide which must not be higher or lower than a certain value. It is also useful to know if a long period of storing causes a deterioration in the organic matter. Infra-red absorption spectroscopy solves this problem easily and rapidly. The general principle of analysis is as follows:

1) Soxhlet extraction of the organic matter to be analysed by a solvent transparent to infra-red.

2) concentration or dilution of the organic matter in the solvent to obtain absorption bands of an intensity comprising between 25 and 75% of rays transmitted. The precision of the measurement of   optical density making it the best at these limited contents.

3) recording of the infra-red absorption spectrum in the region of the characteristic bands and by application of Beer's law, allows us to determine the concentration of the product being studied in the solvent and, hence in the original fertiliser.

a) <u>Determination of Aldrin</u>

We are carrying out in our laboratory the manufacture of a 5-9-10 fertiliser with 0.5% of aldrin. Aldrin or 1-2-3-4-10-10 hexachloro 1-4-4a-5-8-8a hexahydro 1-4 endo exo 5-8 dimethano naphtalene has an infra-red absorption spectrum which is very characteristic and which enables a specific quantitative assessment to be made from its absorption band which is situated at 8.48 microns. The soxhlet extraction of aldrin is made with carbon sulphate; the product of the extraction is concentrated in order to have an aldrin concentration in the CS_2 between 1 and 5%. The infra-red absorption spectrum is recorded between 8 and 9 microns and the optical density, D, of the aldrin band is measured at 8.48 microns. The aldrin concentration in the carbon sulphate is equal to

$$C = \frac{D}{0.405 \times 1}$$

where 1 equals the thickness, in millimetres, of the cell used. The analysis of four samples is finished in one day, including five hours for the soxhlet extraction.

Aldrin is quite stable in a fertiliser. We followed its evolution after a year's storage in different temperature and packaging conditions. We obtained the following results:

Sample	% of aldrin at outset	% of aldrin after 6 months	% of aldrin after 1 year
1	0.51% ± 0.03%	0.55% ± 0.03%	0.52% ± 0.03%
2	0.53% "	0.51% "	0.52% "
3	0.57% "	0.55% "	0.48% "
4	0.60% "	0.52% "	0.53% "

A slight decrease was observed in the amount of aldrin in samples 3 and 4 which had been kept in jute bags. Samples 1 and 2 which had been kept in paper bags were, moreover, very stable.

Determination of lindane

The determination of the gamma isomer of hexachlorocyclohexane is rather difficult for there are 5 isomers of hexachlorocyclohexane of which only the gamma isomer is active, but the simple equation necessary to determine aldrin is replaced by a system of linear equations which enables us to evaluate the influence of the absorption of inactive isomers in the region of the characteristic bands of the gamma isomer at 14.57 microns. Several authors have studied this problem very precisely, and we shall not continue to describe these methods. We are undertaking in our laboratory, the manufacture of a 10-10-10 fertiliser containing 0.2% of lindane. The determination of four samples is completed in one day, including the time taken for soxhlet extraction.

In conclusion we ought to take into account the growing interest which is being given to physical methods in the fertiliser industry, and in particular to the simple and accurate methods of analysis entailed, which enables customers to be provided with well defined fertilisers in which each constituent can be determined.

SUMMARY.

By examining several X-ray diffraction spectra we have been able to determine in phosphate rocks the quantity of quartz and fluorine present, analyses which have enabled us to show in reaction experiments the importance of the chemical nature of silica and also to prove that part of the fluorine occurs in the mineral in the form of fluorine.

By examining X-ray diffraction spectra of phosphatic fertilisers, we have studied the quantity of anhydrite and of hemihydrate in superphosphate. We have studied and identified the nature of potassium and ammonium compounds obtained by the addition of these elements in the form of chloride and sulphate to superphosphate. We have examined several cases, depending on the method of the manufacture of the fertiliser.

By X-ray diffraction we have carried out research on the anion combined with potassium in ternary fertilisers and have followed the stages of the reaction of potassium. This double decomposition is facilitated by the introduction of a liquid phase or by prolonged mechanical action (grinding or mixing).

By infra-red absorption spectrography we have made in our laboratory routine determinations of insecticides (Aldrin - γHCH) added to certain modern fertilisers. This method of determination is particularly interesting because of its speed and specific nature of the material added.