ISMA[*] Technical Conference

Wiesbaden, Germany

11-15 September 1961

---

[*]In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

ISMA

THE INTERNATIONAL
SUPERPHOSPHATE
MANUFACTURERS' ASSOCIATION
TECHNICAL COMMITTEE · COMITÉ DES TECHNICIENS

LE/61/47
Received : 21st March 1961

TECHNICAL MEETINGS - WIESBADEN

CONFIDENTIAL

This paper will be presented at the Technical Meetings in Wiesbaden from September 11th to 15th, 1961. It must not be published prior to that date, and in any case it must not be published without the permission of the author.

THE DETERMINATION OF P_2O_5 IN FERTILISERS : STUDY OF THE VARIOUS EXTRACTION AND DETERMINATION METHODS AND THEIR EFFECTS ON THE ANALYSIS OF SUPERPHOSPHATE-BASED FERTILISERS

by F. Nouyrigat,
Etablissements Kuhlmann, France

SUMMARY

A number of detailed studies have been carried out during the last two or three years in France on the two aspects (extraction and determination) of the analysis of P205 in fertilisers.

A detailed comparison of methods of determination proper has led the A.F.NOR (Association Française de Normalisation - French association for standardisation) to standardise an improved magnesium citrate method which appears to be so precise (both accurate and reproducible) and so generally applicable as to be at present unique.

Following this research it was possible to study the various citrated solutions (Joulie, Petermann and Neutral) and thereby to clarify the main points of divergence.

Thus Neutral citrate was seen to lead to extractions which were relatively unreproducible and unselective.

Petermann citrate appeared to be slightly unfavourable to superphosphate-based fertilisers.

Finally, attention was drawn to the possible existence of condensed forms of P205 which necessitate new methods of determination.

Fundamental differences between the climates and the principal soils and crops in each country have led agronomists and chemists in different lands to develop tests which often differ very considerably not only on a world scale, but also throughout Europe.

The extension of international collaboration is at present greatly hampered by the confusion which never fails to arise when fertilisers are exported or imported.

This confusion, emphasized by frequent analytical disagreement, can only benefit products of doubtful quality.

Several national and international organisations have therefore been recently seeking to undertake studies to bring up-to-date and coordinate the various official methods.

With this in view, a great effort has been made in France in recent years by the laboratories of the main fertiliser manufacturers, both in the field of private enterprise and in the nationalised sector. This work has enabled the Association Française de Normalisation to develop a general and accurate method of analysis of the various forms of P205.

Moreover, an analytical commission representing the main laboratories of the manufacturers of complex fertilisers has been able to carry out a thorough statistical comparison of the main methods over the whole range of French fertilisers. This has recently been published by Jouve (Paris). Detailed examination of this work enables one to draw a number of interesting conclusions concerning the behaviour of superphosphate-based fertilisers as compared with that of fertilisers based on di-calcium phosphate.

1. STUDY OF THE VARIOUS METHODS OF ANALYSIS OF P205 IN FERTILISERS

Any method of analysis of P205 in fertilisers is concerned with two successive stages which are essentially different:

a) Solubilisation by a conventional reagent under conventional conditions.

b) A proper chemical determination of the solubilised P205.

If one wishes to use these methods in all possible cases, one must always bear this duality in mind for fear of being unable to compare the various results on any common basis.

A. METHODS OF DETERMINATION PROPER

Before embarking on any serious study of the processes of solubilisation, we undertook in our laboratories a detailed study of the main methods of analysis.

Two of these have been given particular consideration because of their frequent use in official documents in the various countries.

1. THE MAGNESIUM CITRATE METHOD, at present officially adopted by at least 5 or 6 European countries (cf Table I), has met with considerable criticism in recent years following the demonstration of a certain solubility in the citrate of magnesium ammonium phosphate and a certain coprecipitation of lime.

The work carried out in the Kuhlmann laboratories has enabled us to show that these errors could be counter-balanced in a strict and reproducible manner if the precipitation was made under the proper conditions.

The attached graphs (1 to 4) show clearly the influence of the essential factors in this determination, which are as follows:

the CaO concentration
the citrate concentration
the P_2O_5 concentration.

On the basis of this study the A.F.NOR has prepared a draft standard applicable not only for total P205 but also for water-soluble and citrate-soluble P205.

This draft standard has been checked statistically by nine independent laboratories which have thus provided an incontestable demonstration of its high degree of accuracy (better than 3% relative) and its exceptional reproducibility (0.5% of coefficient of variation) (cf graphs 5 and 6).

2. <u>The Molybdic Methods of the Lorenz type</u>

A parallel study carried out on the precipitation of phosphomolybdate in a sulpho-nitric solution showed that these methods were considerably less advisable, particularly with an extractant containing citrate (cf graphs 7 to 10).

In particular, it seems difficult to design a general method of operation based on this kind of principle.

3. <u>Various more recent Methods</u> appear to be of very considerable interest by virtue of their simplicity or their speed of operation.

The colorimetric methods have much to commend them when analysing in series. The A.F.NOR has recently been studying them in order to determine their accuracy and reproducibility.

It seems that their coefficient of variation must be approximately 1%.

Again, the Perrin method is extremely accurate but must never be applied in the presence of a large number of NH_4+ ions, i.e. in the case of citrate-soluble substances.

B. <u>METHODS OF P2O5 SOLUBILISATION</u>

An examination of table III clearly shows both the basic and the detailed differences which exist between the official texts in the various countries.

This situation has led a number of organisations to undertake general studies of this question, which seems to be thoroughly complicated from the start.

Contrary to the situation regarding methods of analysis, this problem of solubilisation is not wholly chemical, and thus any analytical study can only limit itself to a comparative examination if it is not supported by agronomic experiments, which are alone capable of evaluating the various conventional tests.

The study published by the Analytical Commission of the French complex fertiliser producers was essentially concerned with this problem and afforded a considerable number of most interesting conclusions, the statistical value of which is incontestable : (14 fertilisers - 7 <u>totally independent</u> laboratories.)

1. <u>Water Solubility</u>

The various methods for determing water-soluble P2O5 have led to overall results which are very closely related both from the point of view of value and reproducibility. One should, however, just mention that, in reality, the errors of excess introduced by the Lorenz method of determination mask a slight difference in the amount dissolved between the maceration methods and the systematic French method of extraction which always gives higher results.

This difference is all the more important, as might be expected, when maceration is carried out in a more concentrated medium (the Dutch method).

It is also accentuated by the absence of grinding, which is not allowed for in the German and Dutch methods.

2. Citrate solubility

Unfortunately the same is not true for the determination of citrate-soluble P205, where very considerable differences in reproducibility occur and where, for certain fertilisers (amongst others, "Phospal" fertilisers), there are important analytical variations between the methods themselves and, in the case of certain of these methods, even between laboratories carrying them out.

For other products the overall results, although more varied than for water solubility are, in general, still in apparent and acceptable agreement.

1 - In reality, the appreciable errors introduced by the various methods of analysis mask systematic differences in the actual degrees of solubilisation achieved.

These can be classified in the following order of decreasing values : Dutch (Neutral citrate), French (with one and with two solubilisation stages) (Joulie citrate), and German (Petermann citrate).

It should be noted that, whatever the fertiliser, the difference observed between the French methods, the direct method on the one hand and the once repeated method on the other, is relatively slight, although it is systematically of the same mathematical sign (solubilisation by the direct unrepeated method being slightly greater).

2. A study of the reproducibility of the various methods shows that:

a - The French methods are likely to have the smallest deviation of results.

\- The German method presents results which are slightly more dispersed

c - The Belgian methods (by the Pemberton method of determination) and the Dutch method have a very wide spread of results; the Belgian methods because of their method of determination, since their method of solubilisation is very close to that of the German process, which has a much smaller spread of results. The case of the Dutch method however, cannot be explained by its method of determination which is equivalent to the German method; it seems logical, therefore, to think that it is the Dutch method of solubilisation by Neutral citrate which is responsible for this deviation of results.

II. COMPARISON OF THE VARIOUS OFFICIAL METHODS IN RELATION TO SUPERPHOSPHATE FERTILISERS - (solubilisation by citrates).

It is possible to carry further the examination of the results obtained by the French manufacturers and to make a comparison between the behaviour of superphosphate-based fertilisers and other products, particularly those based on dicalcium phosphate.

The attached table shows that Petermann citrate has a clearly unfavourable effect in relation to the former, since in their case, the Joulie citrate solubilises 5% more P205 in general, whilst this difference is only 1 - 2% for those fertilisers based on dicalcium phosphate which were studied.

Fertiliser	Relative % decrease in solubilisation
18% Superphosphate	4.2%
Ammoniated Superphosphate (without reversion or condensation of P205)	4.6%
Superphosphate-based 10/10/10 fertiliser	6.3%
9/9/12 fertiliser (7.5% of the P205 coming from superphosphate)	4 %
12/16/14 fertiliser (2 - 3% of the P205 from superphosphate)	3 %
Dicalcium phosphate	1.7%
12/12/12 fertiliser based on dicalcium phosphate	1.5%

These results could lead one to suppose a certain solubilisation of reverted P205 by the Joulie citrate alone.

The counter-proof is easy to achieve and has been made on several occasions. If an ammoniated superphosphate is heated and if it is treated with a more or less alkaline constituent (lime for example) reversion, when it occurs, is equally clearly revealed both qualitatively and quantitatively by both Joulie citrate and Petermann citrate.

The neutral citrate, however, continues to include in its determination at least a part of this reverted P205.

An examination of agronomic results published recently by the ONIA (paper presented before the French Academy of Agriculture, Session of 15th June, 1960) fully confirms the value of the Joulie citrate indication (cf Table III).

III. STUDY OF AMMONIATED SUPERPHOSPHATE - CONDENSED P205

The study of certain ammoniated superphosphates has demonstrated that, alongside the classical reverted P205 proper, condensed forms of P205 are also present (pyro- meta- or polyphosphates).

These phosphates can only be determined after prolonged acid hydrolysis. Methods of determination operating in an acid medium hydrolyse these forms of P205 only partially. No agronomic experiments have yet been carried out to determine their actual fertilising value. Thus, until we have fuller information, it is indispensable to distinguish them from orthophosphates.

Only the magnesium citrate method determines them specifically.

A simple modification of the same operating method also renders possible the simultaneous determination of total solubilised P205.

This method has thus brought about the discovery of these various forms in several commercial fertilisers (cf Table IV for example). These other forms of P205 are, at the present time, a not inconsiderable [illegible] of international analytical disagreement.

CONCLUSION

A great deal of work on standardisation has been carried out in recent years in France concerning fertiliser analysis. This work has been accompanied by detailed comparative studies detailing the existing differences between many of the European national methods. These studies have shown, in general, that the various processes for determining water-soluble P205 for fertilisers based on single superphosphate give results which are in substantial agreement.

However, the various citrates, Joulie, Petermann and Neutral (Dutch or American) result in larger differences of solubilisation. In general, the Petermann citrate seems to be unfavourable to superphosphate-based fertilisers. Neutral citrate seems to be of doubtful selectivity, particularly with regard to ammoniated superphosphate.

Apart from the problem of solubilisation, the official methods of determination are far from being completely accurate, reproducible and of general application. The method standardised in France by the A.F.NOR seems, at present, to be the only one suitably embodying these three requirements.

This achievement has been obtained only after experimentation linking a large number of independent laboratories, which is an indispensable condition for valid statistical interpretation.

SLIDE I (TABLE I)

Country	Citrate	Volume of reagent	Weight of Sample	Conditions of Temperature, Agitation & period of reaction	Method of Agitation	Granule Size
FRANCE	Joulie	60 cc	0,750 or 1,500 g according to the fertiliser	As environment. As necessary: 1 hr of agitation, then 12 hrs of rest on water insoluble; or directly on the fertiliser: 3 hrs of agitation + 1 night of rest + 3 hrs of agitation	Mechanical tumbler. 40 t/m.	1 mm. (No. 20) mesh but with <u>grinding in a mortar</u>
BELGIUM	Petermann	100 cc 200 cc	Superphosphate: {1 g if: {P205 > 20% {2 g if: {P205 < 20% Other fertilisers: 1g	18 hrs cold then 1 hr @ 40°C " " N.B.: the cold stage can be replaced by agitation in the mechanical tumbler at the rate of 35 t/mn & at a temperature of 15 - 18°C.	Manually "frequently" or "from time to time" or "several times"	1.5 mm mesh, but with <u>grinding in a mortar</u> except in the case of superphosphate where the acquous extraction residue is put into a Stohmann flask without previous <u>grinding</u>.
GERMANY	Petermann	100 cc	1 g	3 hrs cold with constant agitation, then: 1 hr at 40°C with repeated agitation	Not mentioned	1 mm. mesh, but with grinding in a mortar.
ITALY	Neutral			Methods being worked out		
NETHERLANDS	Neutral	This works on the ratio : <u>Weight of P205</u> Volume of reagent and the volume of the reagent is <u>calculated</u> for each analysis.		Trituration, then three hrs. cold in the tumbler, then 1 hr at 65°C with manual agitation; <u>or</u> no trituation, but 3 hrs at 65°C in the tumbler.	40/50 t/mn mechanical tumbler enclosed at 65°C	1.5 sq. mm. mesh then trituration.

SLIDE 2 (TABLE II)

		Methods of determination of solubilised P205	
	Total P205	Water soluble P205	Water and citrate soluble P205
France	Precipitation of magnesium ammonium phosphate in a citrate medium or: (little used) precipitation of phospho-molybdate and titration in the presence of formol	id	id
Belgium	Precipitation of the phospho-molybdate and titration without formol or: precipitation of the magnesium ammonium phosphate in a citrate medium or: precipitation of the magnesium ammonium phosphate on the redissolution of the phospho-molybdate precipitant	id	id
Germany	Phospho-molybdate precipitate and Lorenz method gravimetry or: magnesium ammonium phosphate precipitation in citrate medium	Superphosphate and its mixtures - precipitation of magnesium ammonium phosphate in citrate medium. For NPK Compound fertilisers and nitrophoska: Lorenz method.	Lorenz method as for total P205
Italy	Former Appiani method: A method of the Jorgensen type. New method: A method of the gravimetric Lorenz method	Methods being modified	
Netherlands	Lorenz method or Jorgensen method	Lorenz method or Jorgensen method	Lorenz method

SLIDE 32 (TABLE III)

Fertiliser	Weight of citrate soluble P205 introduced per pot calculated according to:		Increase of total grain harvest in relation to control without P205, in grams per pot		
	Joulie citrate French method	Neutral citrate Italian method	Date of experiments		
			1958	1959	1954
			Significant differences at P - 0.05		
			2.8	1.5	2.0
Single superphosphate	200 mg	200 mg	14.0	8.2	12.0
French ammoniated superphosphate	200 mg	200 mg			
Foreign ammoniated superphosphate	94 mg	200 mg		2.1	
Complex fertiliser based on ammoniated superphosphate of French manufacture (7% French water and citrate soluble P205)	200 mg	220 mg	12.4		
Complex fertiliser based on ammoniated superphosphate of French manufacture (9% French water and citrate soluble P205)	200 mg	205 mg	12.8		
Phosphal	200 mg	10 to 180 mg			10.5

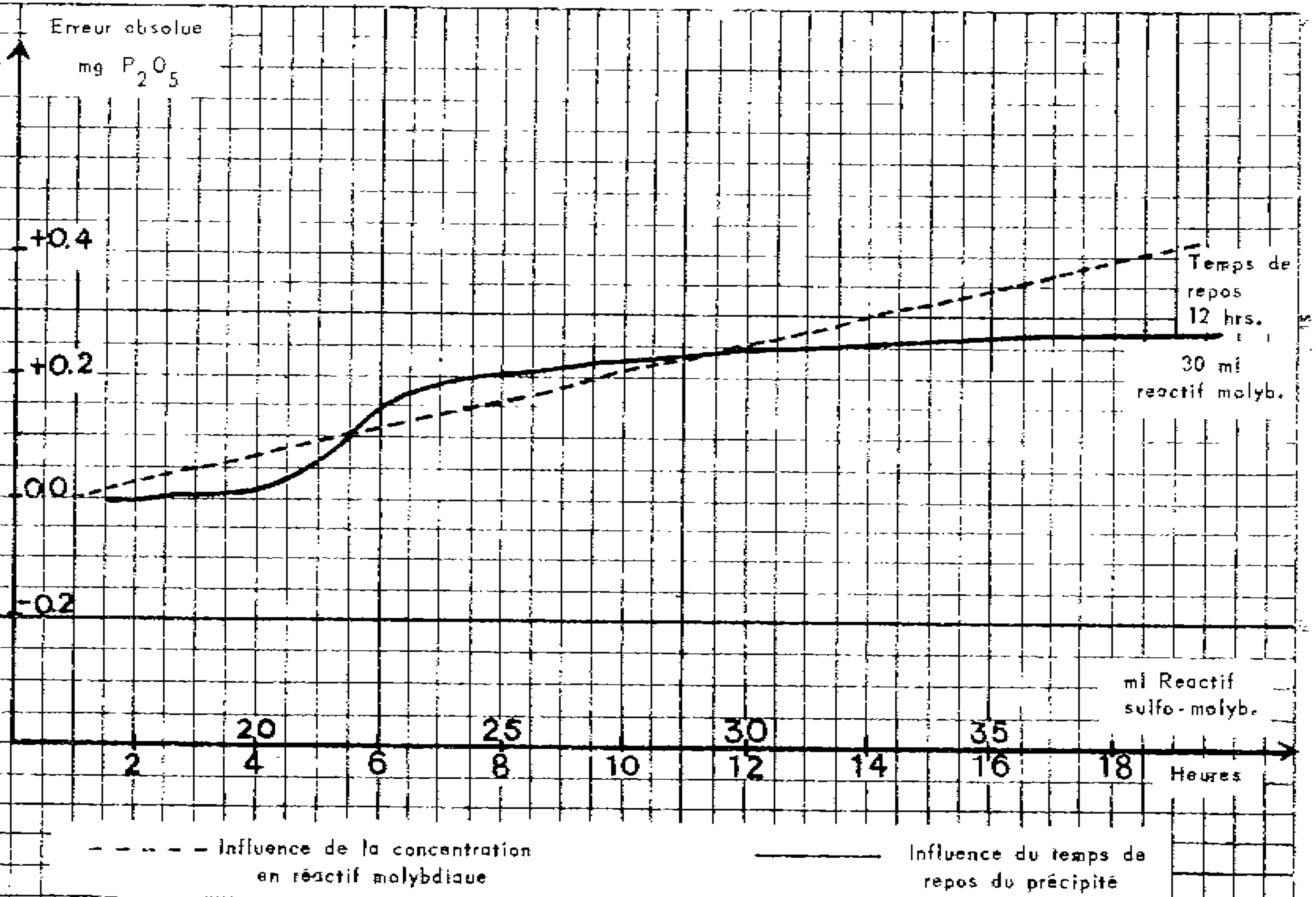
SLIDE 31 - (TABLE IV)

Montecatini (fosfo azoto) 15/30 Fertiliser

Total Water soluble P205	23.9 %
Citrate and water soluble P205 (in orthophosphate form)	24.6 %
Total citrate and water soluble P205	28.6 %
Total P205	30.9 %

giving the following approximate composition:

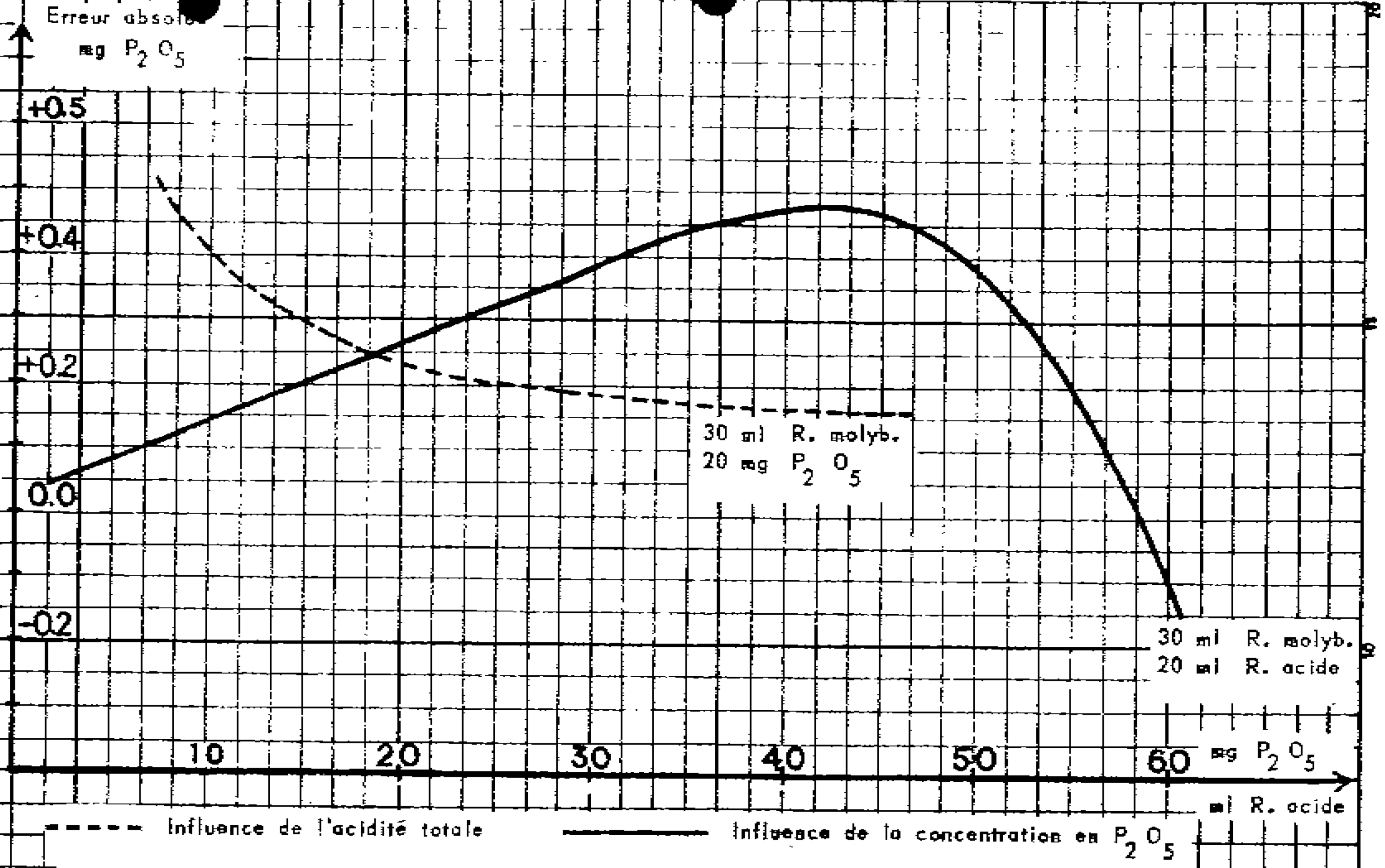
P205 of ammonium and mono-calcium phosphate	24 %
P205 of dicalcium phosphate	0. 6%
P205 in the form of citrate soluble condensed phosphate of lime	4 %
Insoluble P205	2.4 %



(Volume total : 70 ml - 20 mg P_2O_5 - 20 ml réactif acide)

PROJECTION 16 (Courbes 10)

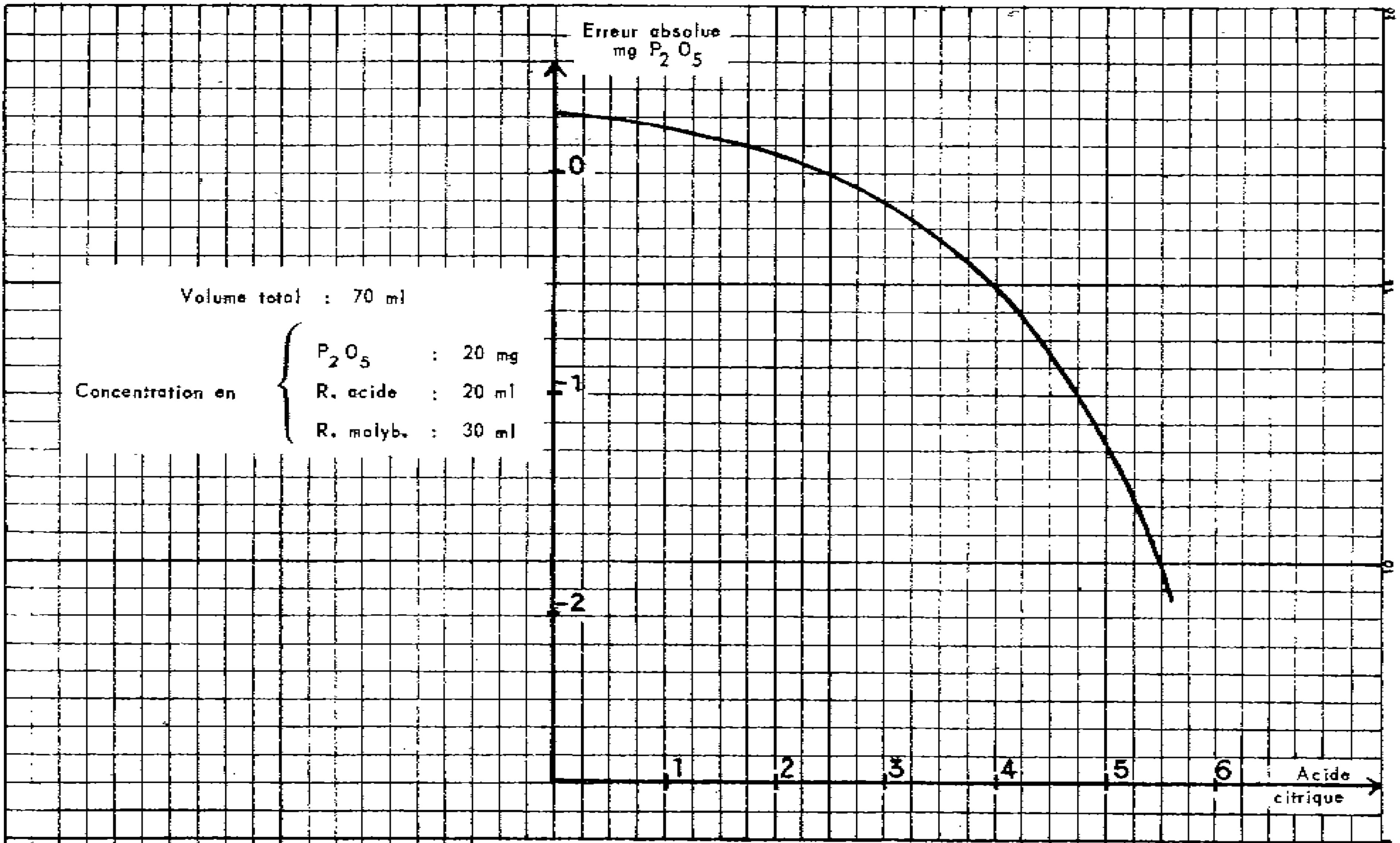
Méthode Lorenz : Concentration en Réactif Molybdique



(Volume total : 70 ml)

PROJECTION 15 (Courbes 9)

Méthode Lorenz : Concentration en P_2O_5 et Acidité totale

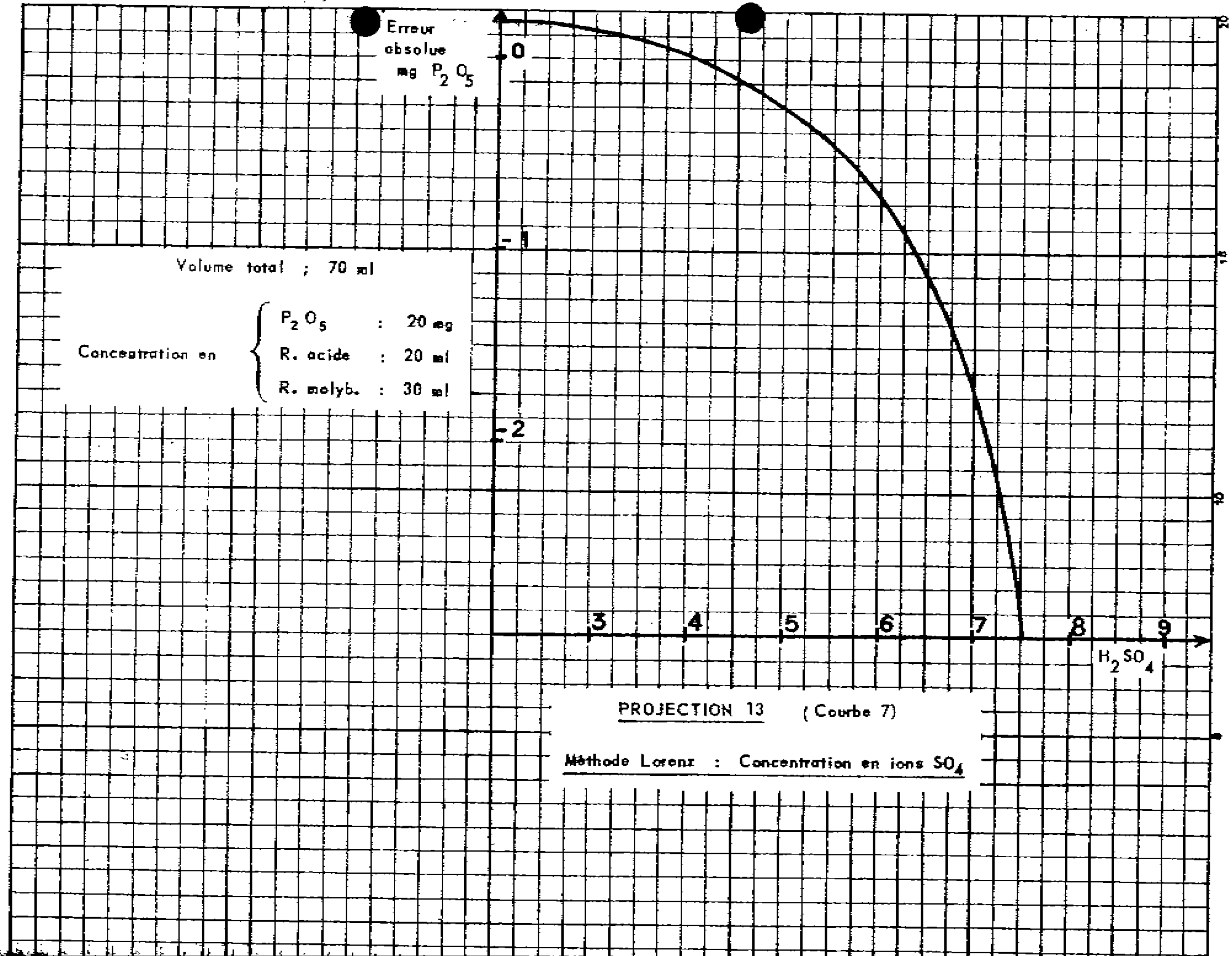


Volume total : 70 ml

Concentration en
P_2O_5 : 20 mg
R. acide : 20 ml
R. molyb. : 30 ml

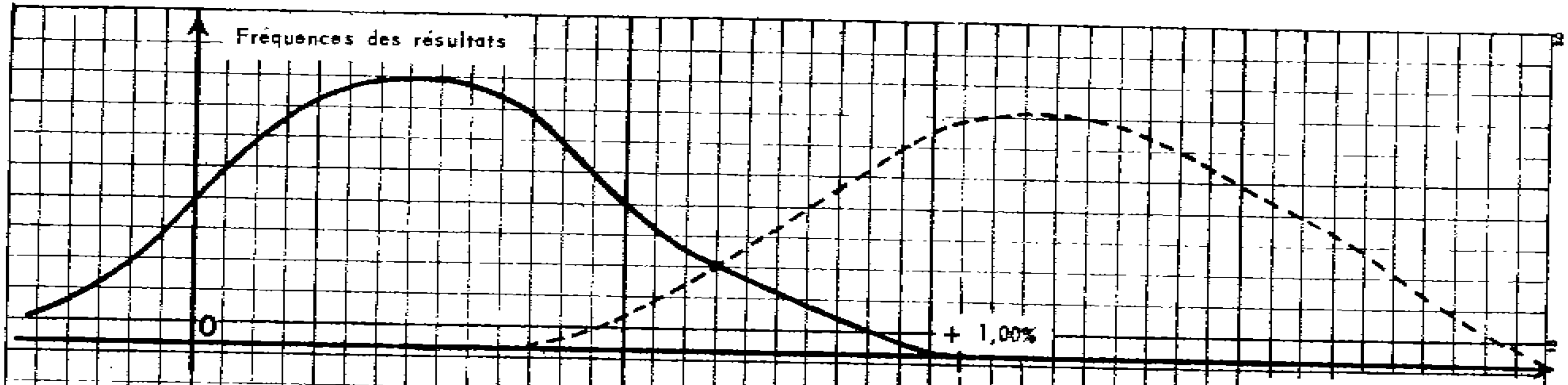
PROJECTION 14 (Courbe 8)

Méthode Lorenz : Concentration en ions citriques

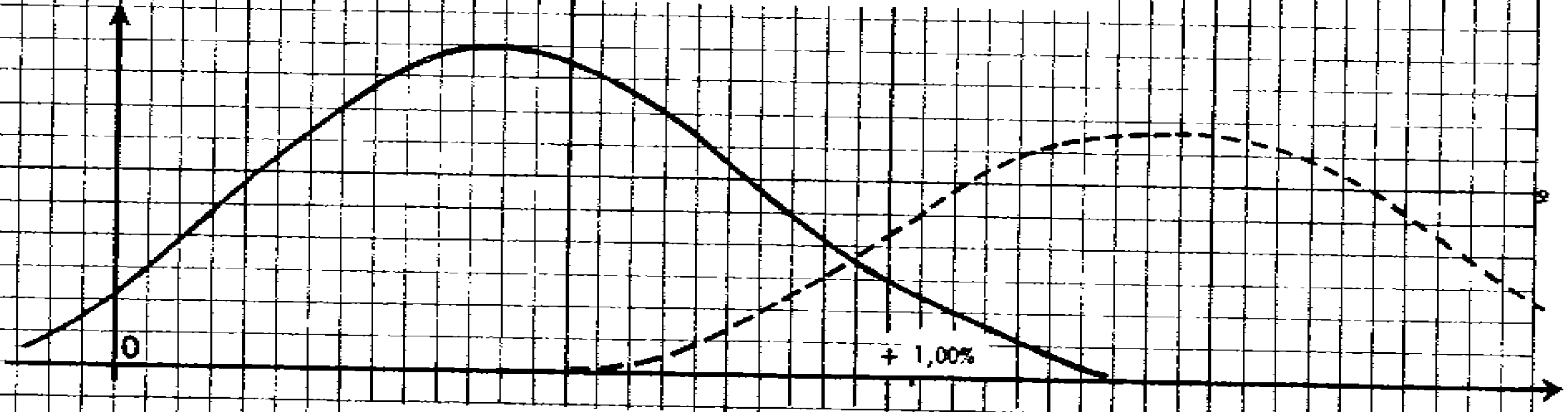


PROJECTION 13 (Courbe 7)

Méthode Lorenz : Concentration en ions SO_4



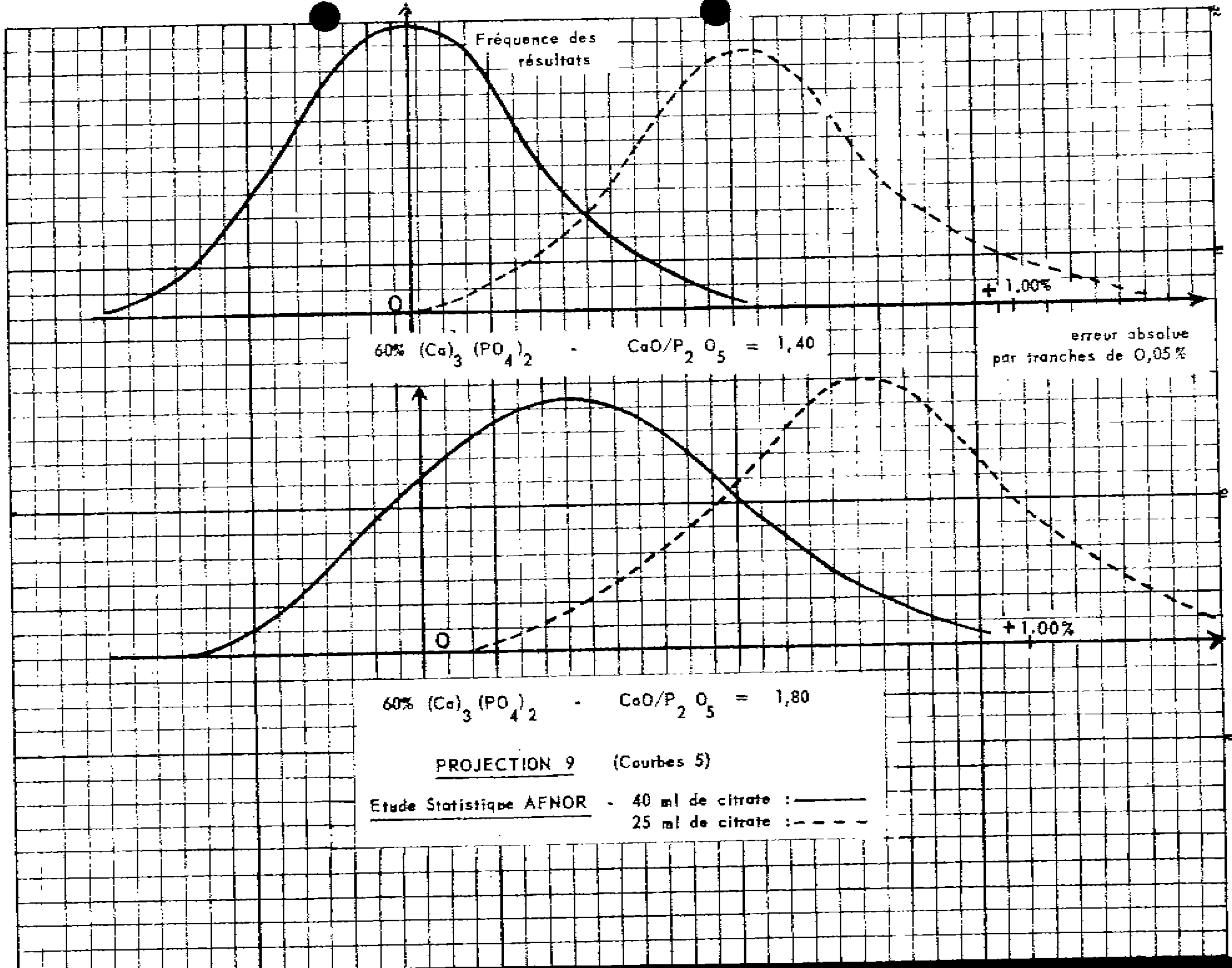
80% $(Ca)_3(PO_4)_2$ - $CaO/P_2O_5 = 1,40$



80% $(Ca)_3(PO_4)_2$ - $CaO/P_2O_5 = 1,80$

PROJECTION 10 (Courbes 6)

Etude statistique AFNOR - 40 ml citrate : ———
25 ml citrate : - - - - -

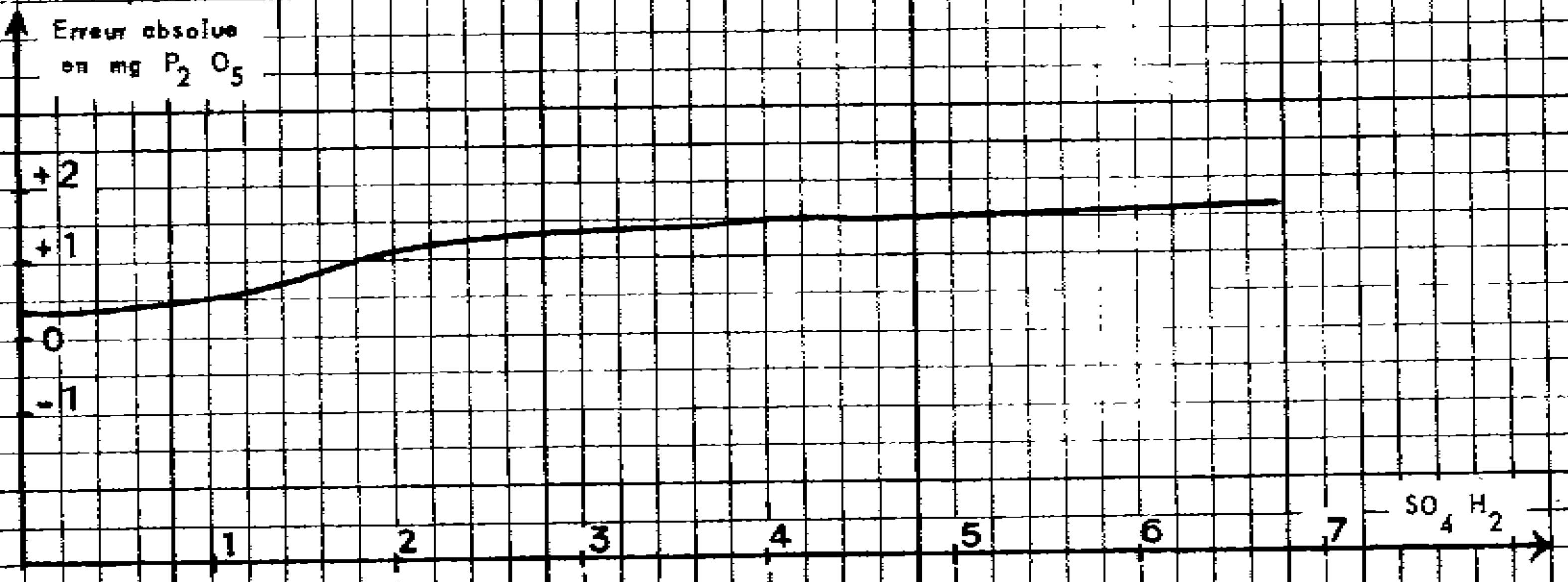


60% $(Ca)_3(PO_4)_2$ - CaO/P_2O_5 = 1,40

60% $(Ca)_3(PO_4)_2$ - CaO/P_2O_5 = 1,80

PROJECTION 9 (Courbes 5)

Etude Statistique AFNOR - 40 ml de citrate : ———
25 ml de citrate : - - -



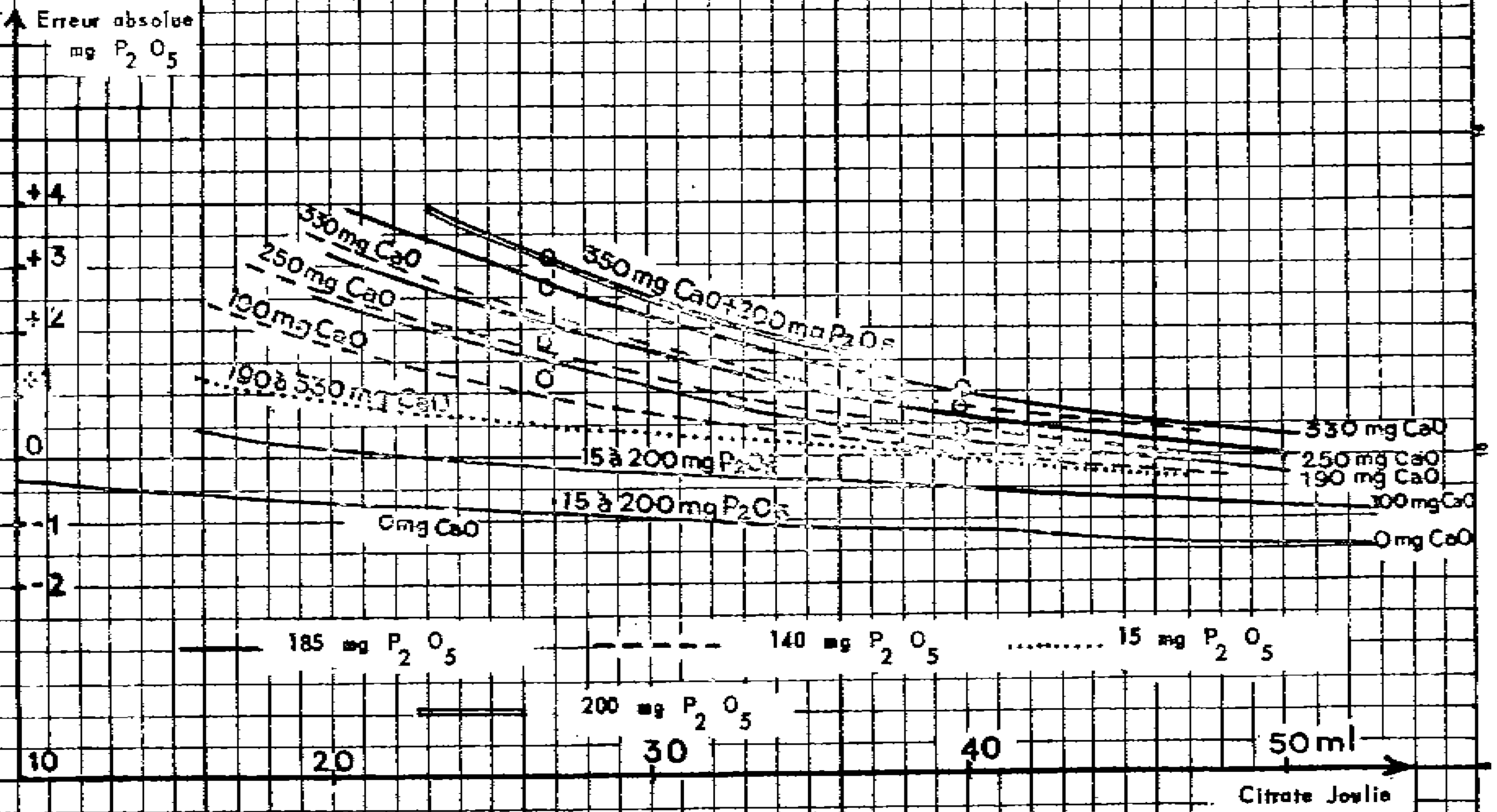
Volume total : 200 ml

Concentrations : en P_2O_5 - 175 mg ; en CaO - 200 mg ; en MgO - 300 mg

Ajoute de citrate Joulie - 40 ml

PROJECTION 12 (Courbe 4)

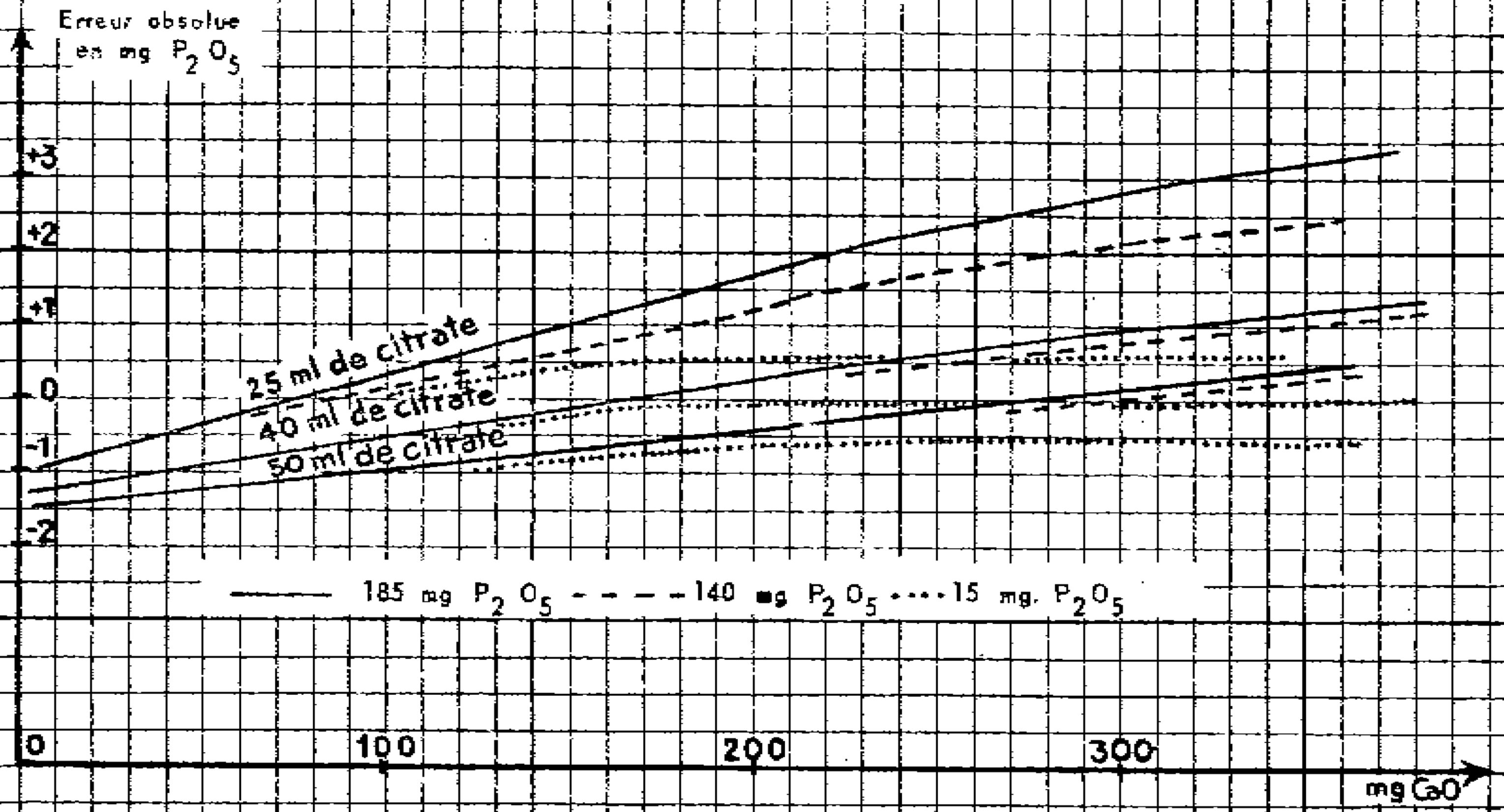
Méthode Citromagnésienne : Concentration en SO_4^{--}



Volume Total : 200 ml - Concentration en MgO : 300 mg

PROJECTION 7 (Courbes 3)

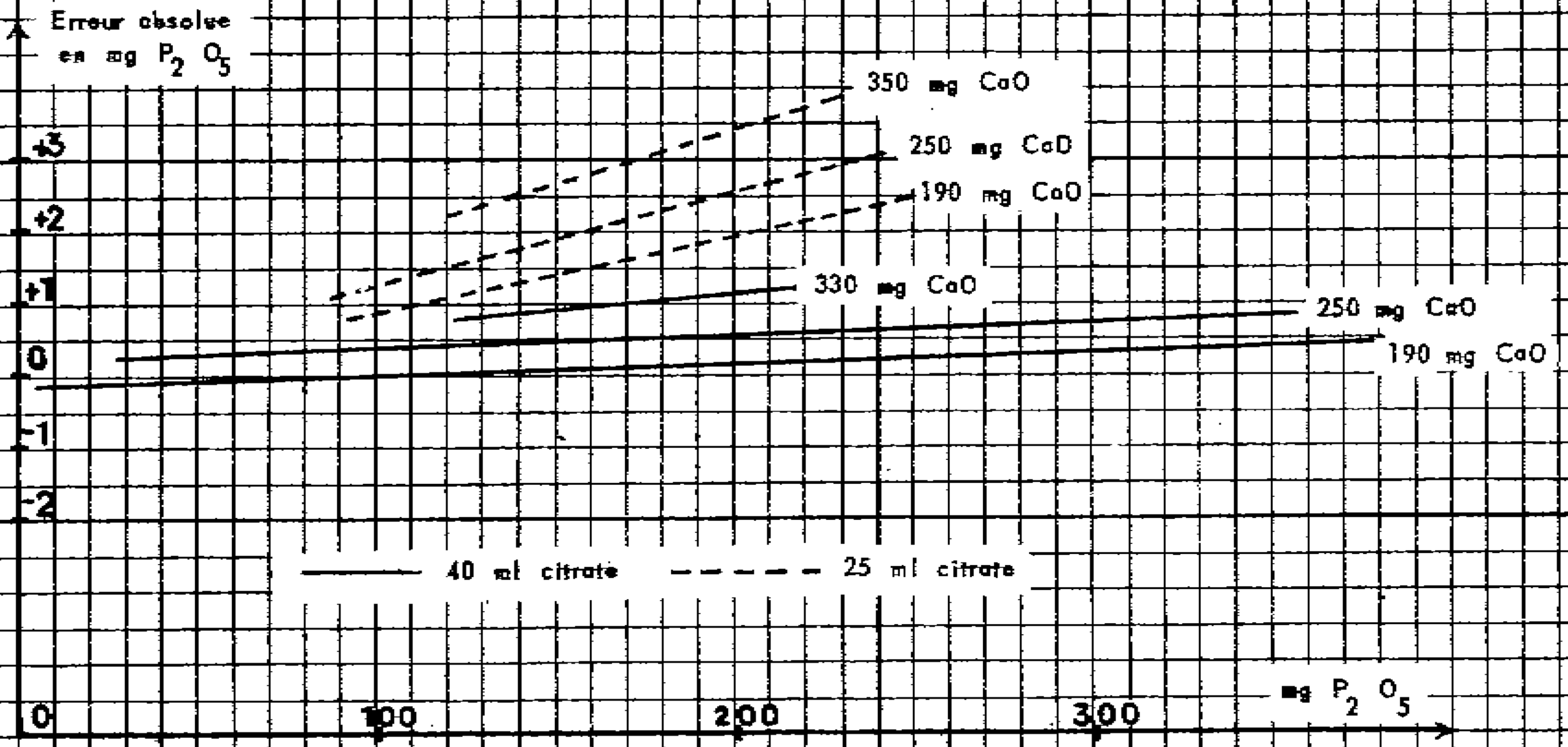
Méthode citromagnésienne : Influence des teneurs en citrate



Volume Total : 200 ml - Concentration en MgO : 300 mg

PROJECTION 6 (Courbes 2)

Méthode citromagnésienne - Influence de la concentration en CaO



Volume total : 200 ml - Concentration en MgO : 300 mg

PROJECTION 5 (Courbes 2)

Méthode citromagnésienne : Influence de la concentration en P_2O_5