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FACTORS INFLUENCING THE REPRODUCIBILITY OF ISOTACHOPHORETIC DETERMINATIONS OF IONS PRESENT IN WET-PROCESS PHOSPHORIC ACID*

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SUMMARY

Factors affecting the precision of quantitative isotachophoretic analysis in general and also those which must be taken into account in the analysis of wet-process phosphoric acid were investigated in order to achieve a reproducibility of the determination of phosphate in this material characterized by a coefficient of variation (C.V.) in the range 0.1–0.2%.

Adsorption of phosphate on the walls of the sample-delivering container was the main source of analytical errors in the determinations of this constituent. This loss of analyte was eliminated by the addition of cetyltrimethylammonium bromide to the sample solution and by using a container having a small surface-to-volume ratio. Proper adjustment of the pH of the sample solution was also important, especially for achieving adequate reproducibility in the quantitation of sulphate.

Under optimal analytical conditions sulphate, fluoride, phosphate, iron and aluminium present in wet-process phosphoric acid could be simultaneously determined from their electronically measured zone lengths. C.V. values of 0.1–0.2% were obtained for the determinations of phosphate and those for the other constituents ranged from 0.3 to 2.2% in a series of analyses. The same reproducibilities of the determinations of the constituents were achieved for wet-process phosphoric acid treated with HNO₃ when analysis in two operational systems was a preferable analytical alternative.

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INTRODUCTION

Wet-process phosphoric acid is produced in huge amounts, especially for use in universal fertilizers. As both phosphoric acid and universal fertilizers are the subjects of intense commercial activity, analyses of the constituents present in these materials are carried out in laboratories involved in process control and in the establishments responsible for quality assurance.

Gravimetric methods for the determination of phosphate in both phosphoric acid and fertilizers are preferred when both high accuracy and high precision are essential. Many papers have been devoted to this subject and an excellent overview was given by Williams¹. The quinoline molybdophosphate gravimetric method is regarded as the most suitable for the determination of phosphate in the above materials and its use is accepted by the International Organization for Standardization (ISO), by the Association of Official Analytical Chemists as a final action method and by many national standards institutes (see, *e.g.*, refs. 2–4). The results of two parallel determinations using this method should not deviate by more than 0.2% for 5–10% contents of P₂O₅ or by more than 0.4% for 10–50% contents of P₂O₅ (ref. 4).

Of the other anionic constituents in wet-process phosphoric acid, fluoride and sulphate are often determined. Fluoride is mostly determined either by a spectrophotometric alizarin fluorine blue method^{5–7} or with ion-selective electrodes^{8–10}. The former method is also accepted by ISO¹¹.

Sulphate present in the acid can be determined gravimetrically as BaSO₄ or more often by titrimetry after reduction of sulphate to hydrogen sulphide (ref. 1, p. 529). The latter method is recommended by ISO for the determination of sulphate in phosphoric acid for industrial use¹².

Ca²⁺, Fe³⁺, Al³⁺ and Mg²⁺ are the most abundant cations in wet-process phosphoric acid. Some of them form strong complexes with anionic constituents (Fe³⁺, Al³⁺ with F⁻ and PO₄³⁻) and in many instances also precipitates (CaSO₄, phosphates of calcium, iron, aluminium, etc.), thus making sample pre-treatment before the analysis necessary. Therefore, the complete analysis of wet-process phosphoric acid is divided into several procedures in which each of the constituents is determined separately. An obvious disadvantage of such an approach is a long time delay between the sampling and the end of complete analysis. Moreover, these analytical procedures are labour consuming and their replacement by rapid and simpler method(s) is desirable in process control laboratories.

To overcome some of these drawbacks, we studied the possibility of using capillary isotachopheresis (ITP) for the analysis of anionic constituents present in wet-process phosphoric acid. We had to solve several partial problems to achieve the desired analytical aim. For example, the separation conditions under which the complex formation between the sample constituents does not interfere in the determinations of both phosphate and the microconstituents were investigated¹³.

When the optimal operational system found in this investigation (see Table I) was applied to the analysis of model mixtures having a composition identical with that of wet-process phosphoric acid and, simultaneously, to the analysis of pure constituents, the results of quantitation agreed very well. Typically, the mean results of ITP determinations of phosphate present in such mixtures coincided with the

corresponding mean values obtained for the pure constituents with 0.1–0.4% relative deviations, which were considered to be statistically insignificant. A similar agreement between the results of quantitative analyses was obtained when ITP and gravimetry were compared for the analysis of the same samples of phosphoric acid. In other words, ITP provided sufficiently accurate analytical results meeting the requirements accepted for the quinoline molybdophosphate gravimetric method⁴.

However, the coefficients of variation (C.V.) for parallel ITP runs were 2–3 times higher than those of parallel gravimetric determinations (0.1–0.2%). Therefore, it was necessary to improve this performance characteristic of ITP determination before a detailed comparative study of the methods was initiated. As a precision of quantitation characterized by a C.V. of 0.1–0.2% is not common in ITP, we studied the factors that are of general importance in quantitative ITP analysis and those which must be considered in the determination of phosphate. The results of this study are presented in this paper.

EXPERIMENTAL

Instrumentation

A CS Isotachophoretic Analyser (VVZ PJT, Spišská Nová Ves, Czechoslovakia) was assembled in column-coupling configuration of the separation unit^{14,15} using modules provided by the manufacturer. Moreover, a special buffering chamber was mounted between the refilling block for the pre-separation column and the bifurcation block to increase the volume of the channels between the membrane and the column (a detailed description of the instrument will be given elsewhere). In all experiments the samples were introduced into the separation unit of the analyser with the aid of a sampling valve, which is an integral part of the sample injection system of the above instrument.

As a very precise zone length measurement was an essential requirement in this work, the analyser was provided with an electronic stop-watch coupled to a printer (see below).

Chemicals

As impurities present even in very small amounts in the leading and terminating electrolyte solutions can have an undesirable influence on the zone length(s), especially when their amounts change from run to run, we used triply distilled water for the preparation of these solutions. The anionic purities of the solutions were improved when a small amount of KMnO_4 was added to water in the last distillation step.

Histidine was obtained from Reanal (Budapest, Hungary), morpholinoethanesulphonic acid (MES) from Sigma (St. Louis, MO, U.S.A.), triethylenetetramine (TETA) from Spolchemie (Ústí, Czechoslovakia), caproic acid and cyclohexanedi-aminotetraacetic acid (DCTA) from Lachema (Brno, Czechoslovakia), cetyltrimethylammonium bromide (CTABr) from Serva (Heidelberg, F.R.G.) and Natrosol 250 HR hydroxyethylcellulose from Hercules (Rijswijk, The Netherlands).

Histidine and MES were purified by repeated precipitation (dissolution in water purified in the above manner and precipitation with doubly distilled acetone). Caproic acid was purified by repeated extraction with water. Anionic impurities in TETA were removed by an anion exchanger in the OH^- form.

RESULTS AND DISCUSSION

Some factors influencing the reproducibility of quantitation in ITP

When a high reproducibility of ITP determinations is required, all factors that adversely influence the migration velocity in the steady state must be eliminated or well controlled. Convective flows in the separation compartment represent a possible source of such disturbances. They can be due to leaks in the separation compartment when insufficiently tight connections and closing valves are used or when the membranes are leaky. In this work variations in such flows as small as 250 pl/sec could lower the reproducibility of the determination of phosphate (see below). Another source of convective flows of this kind is the movement of the membranes and we prevented this as described elsewhere¹⁶.

Electroosmosis is a phenomenon that is always associated with electrophoretic separation. Convective disturbances due to electroosmosis in ITP were recently studied in detail by Reijenga *et al.*¹⁷. Of the possible alternatives for minimizing its influence¹⁷, we preferred the suppression of the zeta potential using non-ionic HEC.

When a high driving current is applied, thermal convection can have a deteriorous effect on the zone boundaries¹⁸, resulting in a decreased reproducibility of quantitation. To minimize the effect of this phenomenon we used adequate driving currents and, moreover, the use of HEC as an anticonvective additive also suppressed thermal convection to a certain extent¹⁸.

The same solution of the leading electrolyte as used for the separation was provided in the counter-electrode compartment to eliminate osmotic flows through the membrane. In spite of the fact that in many instances this can be neglected, we could generate a counter flow of the solution in the separation compartment (having a velocity equal to 5–10% of the migration velocity) when the leading electrolyte in the capillary tube contained 1% of glycerine whereas that in the counter-electrode compartment did not.

Short-term and/or long-term irreproducibilities of the driving current also contribute to the changes in the migration velocity of the separands. These can be eliminated, *e.g.*, by coulometric recording¹⁹. However, the short-term current stability of the power supply used in this work was better than 0.01% of the adjusted value for one decade changes in load. The long-term current stability (day-to-day stability) was better than 0.1%²⁰.

Other sources of decreased reproducibility of quantitation in ITP are associated with the electrode reactions at the counter electrode and/or the different selectivity of the membrane for different counter ions when the volume capacity of the channel between the membrane and the column is not sufficient. This possible source of errors (a change in the migration velocity during the analysis) was eliminated in this work through the use of an additional buffering chamber (see Experimental).

The role of impurities present in both the leading and terminating electrolyte solutions in quantitative ITP analysis is well known²¹ and thorough deionization of the water and purification of the chemicals used for the preparation of these solutions was essential in this work (see Fig. 4).

The reproducibility with which the sample is injected is important when very precise analytical results are required. We preferred the use of a valve at least for two reasons. A valve provides very reproducible sample delivery between the solutions

of leading and terminating electrolytes and as the anions of interest form strong complexes with Fe^{3+} (ref. 22), any contact of the sample solution with metallic parts could thus be avoided.

The above factors are of general importance when very reproducible ITP determinations are required. Disturbances caused by them could be evaluated in this work through a decreased reproducibility of the time of entry of the first zone into the detector of the pre-separation column and through a continuous or sudden change of this time. Obviously, a decreased reproducibility of the zone length(s) was also indicative in this respect. When all the above disturbances were eliminated or suppressed, the coefficient of variation of the time of entry of the first zone into the detector in runs lasting 500 sec was in the range 0.04–0.06%.

Zone length measurement

As the analyser used in this work is not provided with an electronic stop-watch suitable for zone length measurement, we had to develop such a device. The zone lengths were measured with the aid of a.c. conductimetric detectors. These detectors provide staircase-like waveforms on the output of the linear signal (LIN) and the inflection points are related to the zone boundaries^{21,23}. The zone boundaries are also represented by the peak apexes of the differential signal (DIFF). This signal is an absolute value of the first derivative of the signal LIN. In order to achieve an accurate determination of the peak apex, the signal DIFF is differentiated. The peak apex of the signal DIFF is then related to the negative transition across the zero-line of this derivative²³ and it can be handled by digital circuits. For these reasons, we used the DIFF signal of the conductivity detectors for the stop-watch control.

Depending on the complexity of the mixture to be separated, the peaks from the DIFF output can be high and/or steep or else small and/or flat. When the signal DIFF passes through the usual passive differentiator formed by an RC network, the output reaction is affected by a phase error due to the voltage over-resistance R^{23} . When the DIFF signal passes through an active differentiator (Fig. 1a), a correct output reaction is obtained only for a small range of peak steepness. For very steep peaks the active differentiator becomes saturated and a certain time is necessary for its recovery. On the other hand, for flat peaks its output reaction is poor and the signal disappears in the noise.

To overcome the above disadvantages we used an active differentiator with non-linear feedback for the processing of the signal DIFF (Fig. 1b). This solution enables a wide dynamic range of the input signal waveform to be handled. A Zener diode is used in the feedback for two purposes: it prevents the saturation of the differentiator and determines the output voltage levels for TTL circuits. The performances of both circuits were compared using a triangular input voltage as the peak apex of this waveform is clearly defined and its steepness can be changed easily (see Fig. 1).

A threshold comparator gates the CLK signal for a low DIFF signal (Fig. 2), thus improving the noise immunity of the system. A time error due to the signal quantization is ± 1 msec for a 1 kHz frequency or ± 10 msec for a 100 Hz frequency. TIMER suppresses the record of the zones shorter than a pre-selected time interval (1, 2, 4, 8, 16 and 32 sec on our stop-watch). In this instance a buffer for a printer having a printing capability of one line per second need not be used. The flow chart in Fig. 3 describes the function of the stop-watch.

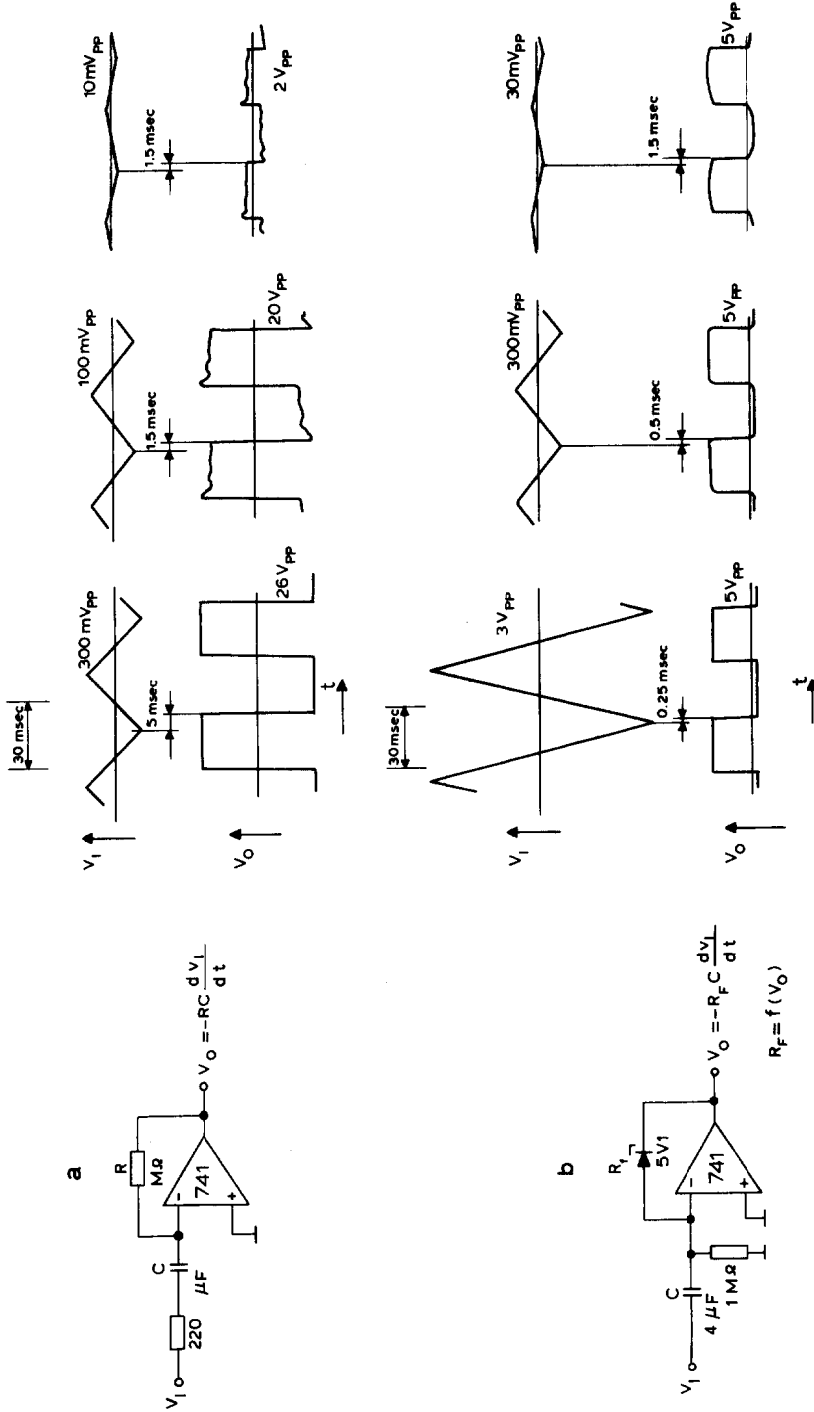


Fig. 1. Comparison of performances of differentiators used for processing the differential signals from the conductivity detectors. (a) Active differentiator; (b) differentiator with non-linear feedback (for further details, see text).

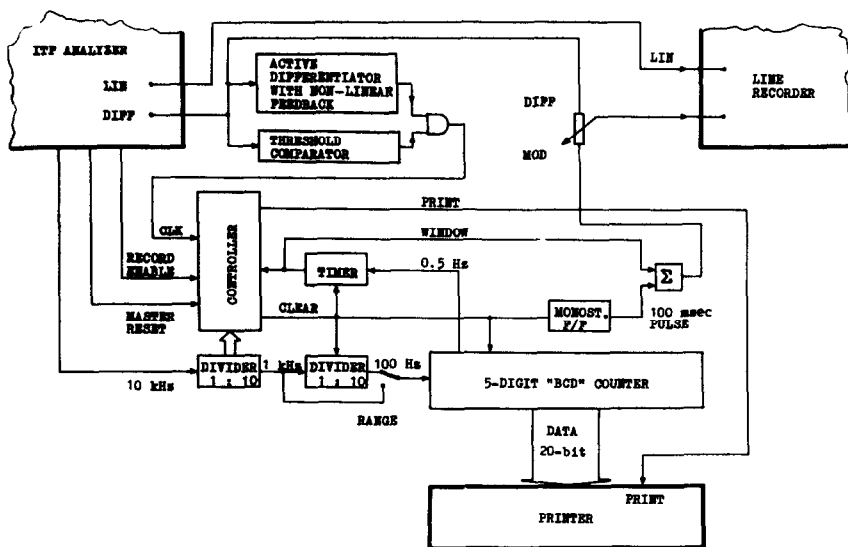


Fig. 2. Schematic diagram of electronic stop-watch used for the zone length measurement from the conductivity detector.

The differentiator with non-linear feedback is capable of processing peaks having slopes in the range $0.3\text{--}1500\text{ Vsec}^{-1}$ with an accuracy of $0\text{--}2\text{ msec}$. The total accuracy of the time interval (zone length) measurements is $-1, +3\text{ msec}$ for a 99.999 sec display format ($-10, +12\text{ msec}$ for a 999.99 sec display format). These accuracies are related to the DIFF signal. Our results of quantitative analysis (see below) and

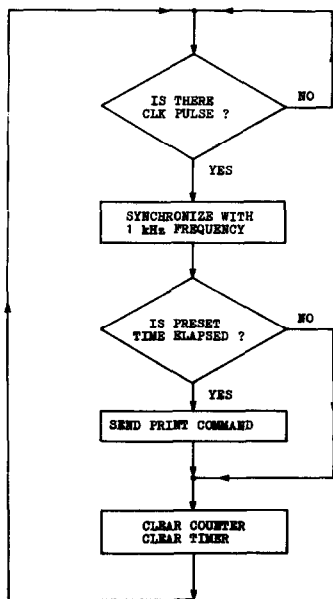


Fig. 3. Flow chart describing the function of the stop-watch shown in Fig. 2.

the results achieved in other laboratories²⁴ show that a zone length measurement with such a precision is not only justifiable but seems necessary in ITP because this method enables a high reproducibility of quantitation to be achieved.

Factors affecting the reproducibility of quantitation of ionic constituents present in wet-process phosphoric acid

The factors that are of general importance in quantitative ITP analysis were discussed above. In the analysis of model mixtures relevant to wet-process phosphoric acid we found several factors that can adversely affect the quantitation of one or several constituents, and these will be dealt with in this section.

Different chelating agents were tested as additives to the sample to convert Al^{3+} and Fe^{3+} into chelates migrating anionically. This step in the analysis was necessary as both cations form strong complexes with fluoride and phosphate. In conjunction with these experiments a large number of operational systems was investigated (the variable parameters being pH, counter ions and co-counter ions). The best results were achieved when cyclohexanediaminotetraacetic acid (DCTA) was added to the sample when the pH of the leading electrolyte was higher than *ca.* 5.5, and the operational conditions used in this work (Table I) seem optimal in many respects¹³.

TABLE I
OPERATIONAL SYSTEMS

| Parameter | System No.* | |
|-------------------------------------|-------------|-----------|
| | 1 | 2 |
| Solvent | Water | Water |
| Leading anion | Cl^- | Cl^- |
| Concentration (mM) | 10 | 10 |
| Counter ion | HIS^+ | HIS^+ |
| Co-counter ion | — | TETA |
| Concentration (mM) | — | 2 |
| Additive to the leading electrolyte | HEC, 0.1% | HEC, 0.1% |
| pH of leading electrolyte | 5.70 | 5.65 |
| Terminating anion | MES | CAPR |

* CAPR = caproic acid; other symbols as in Experimental.

In the analysis of model mixtures of anionic constituents that need to be determined in phosphoric acid (SO_4^{2-} , F^- , PO_4^{3-}), we found a gradual decrease in the length of the zone of phosphate when the sample (of pH 6.0) was introduced into the valve from the same sample solution kept in a polyethylene syringe (a 4% relative decrease after three consecutive runs). The zone lengths for the other constituents remained unaffected. A thorough evaluation of this decrease showed that phosphate was lost as a result of adsorption on the walls of the syringe. This, however, is a general property of phosphate (ref. 1, p. 445) and when we added CTABr to the sample at a concentration of 10^{-5} M the loss of the analyte was eliminated because of preferential adsorption of CTA^+ .

To optimize further the conditions of sample handling, we studied the influence of the volume of the polyethylene syringe from which the sample is delivered into the injection valve. A model mixture containing 0.5 mM acetate, 0.5 mM formate, 2 mM phosphate and 10 μ M CTABr with the pH adjusted to 6.0 was delivered into the valve using either a 2- or a 20-ml syringe. To exclude all other factors that could introduce doubts into the interpretation of the results, the measurements were carried out as a series in which the two syringes were alternately changed for sample delivery, using the same sample solution (kept in a Simax volumetric flask). Three runs were performed from each syringe refilling, always displacing the same volume of the sample. Five series of runs were carried out for each syringe. The zone lengths of phosphate as measured by the electronic stop-watch are summarized in Table II.

TABLE II

INFLUENCE OF THE VOLUME OF THE SAMPLE CONTAINER ON THE ZONE LENGTH OF PHOSPHATE

Zone lengths are given in seconds.

| Syringe* | Series No. | Run No. | | | Z(3) | S.D. | C.V.(%) |
|----------|------------|---------|-------|-------|-------|------|---------|
| | | 1 | 2 | 3 | | | |
| 2 ml | 1 | 38.44 | 38.37 | 38.36 | 38.39 | 0.04 | 0.10 |
| | 2 | 38.54 | 38.20 | 38.30 | 38.35 | 0.17 | 0.44 |
| | 3 | 38.48 | 38.31 | 38.29 | 38.36 | 0.10 | 0.26 |
| | 4 | 38.47 | 38.27 | 38.20 | 38.31 | 0.14 | 0.37 |
| | 5 | 38.53 | 38.27 | 38.22 | 38.34 | 0.17 | 0.44 |
| Z(5) | | 39.49 | 38.28 | 38.27 | | | |
| S.D. | | 0.04 | 0.06 | 0.07 | | | |
| C.V.(%) | | 0.10 | 0.16 | 0.18 | | | |
| 20 ml | 1 | 38.43 | 38.38 | 38.38 | 38.40 | 0.03 | 0.08 |
| | 2 | 38.40 | 38.44 | 38.40 | 38.41 | 0.02 | 0.05 |
| | 3 | 38.43 | 38.44 | 38.46 | 38.44 | 0.02 | 0.05 |
| | 4 | 38.49 | 38.43 | 38.43 | 38.45 | 0.04 | 0.10 |
| | 5 | 38.45 | 38.38 | 38.42 | 38.42 | 0.04 | 0.10 |
| Z(5) | | 38.44 | 38.41 | 38.42 | | | |
| S.D. | | 0.03 | 0.02 | 0.04 | | | |
| C.V.(%) | | 0.08 | 0.05 | 0.10 | | | |

* 2-ml syringe: Z(15) = 38.35; S.D. = 0.12; C.V. = 0.30%. 20-ml syringe: Z(15) = 38.42; S.D. = 0.03; C.V. = 0.07%. Z(n) = mean zone length for n runs; S.D. = standard deviation; C.V. = coefficient of variation.

A small decrease in the length of the phosphate zone is apparent when we compare the first runs with the following ones for the 2-ml syringe. A statistical treatment of these data using a *t*-test (ref. 25, p. 42) classifies the first runs for this syringe volume as deviating statistically with a high significance. The results for the 20-ml syringe did not exhibit such deviations. Moreover, when the coefficients of variation for the zone lengths of phosphate were compared for the two syringes, favourable results were provided by the 20-ml syringe. The difference in the mean values obtained with the two syringes in fifteen runs (0.2% relative deviation) was

evaluated as statistically significant. Undoubtedly, this deviation can be explained through the adsorption of phosphate, which is more important in a small-volume container having a less favourable surface-to-volume ratio. Reference constituents (formate and acetate) did not exhibit such behaviour.

In order to minimize the possibility of hydrolysis of Fe^{3+} and Al^{3+} during the sample handling we analyzed model mixtures having a composition close to that of wet-process phosphoric acid and differing only in the pH of the injected solutions. Surprisingly, a severe decrease in the reproducibility of the determination of sulphate occurred when the pH of the injected solution was lower than *ca.* 4. Investigations of this irreproducibility revealed that it occurs only in the determination of sulphate in the presence of phosphate. This observation was confirmed by the analysis of mixtures containing only these anions when the pH of the injected solution was the only variable (see Table II). There appears to be no explanation for this behaviour of sulphate in the presence of phosphate. However, in view of these findings, we analysed samples with the pH adjusted to 5.5–6.0.

TABLE III

INFLUENCE OF THE SAMPLE pH ON THE REPRODUCIBILITY OF DETERMINATION OF SULPHATE AND PHOSPHATE

| <i>Anion</i> | <i>pH of sample</i> | <i>Z(11)*</i> (<i>sec</i>) | <i>S.D.*</i> (<i>sec</i>) | <i>C.V.*</i> (%) |
|--------------|---------------------|---------------------------------|--------------------------------|---------------------|
| Sulphate | 2.6 | 4.58 | 0.43 | 9.4 |
| Phosphate | 2.6 | 39.83 | 0.16 | 0.4 |
| Sulphate | 5.9 | 3.43 | 0.03 | 0.9 |
| Phosphate | 5.9 | 38.68 | 0.08 | 0.2 |

* Symbols as in Table II.

Analysis of wet-process phosphoric acid

Practical samples of the acid containing a precipitate or free of it (see Introduction) were analysed to evaluate the reproducibilities of ITP determinations of the constituents of interest. For obvious reasons, in these analyses we followed strictly all the above requirements necessary to achieve a high reproducibility of quantitation.

Operational system No. 1 (Table I) was used for complete anionic analysis of the acid when it was free of the precipitate and it also served for the quantitations of phosphate, fluoride, iron and aluminium when the precipitate was present (see below). The anionic purity of the operational system was always checked before a series of analyses, once during the sample analyses and at the end of the series. Isotachopherograms from both the pre-separation and analytical columns taken from such a purity control are shown in Fig. 4. We found that impurities present in the system (see the isotachopherogram from the analytical column) originated mainly from water and their zone lengths changed negligibly not only within a series of analyses but also over a long period when the same solvent source was used. As none of the detected impurities migrated with an effective mobility identical with that of phosphate, only a small systematic bias was introduced into its quantitation owing to their continuous migration through the zone of phosphate. This bias can be com-

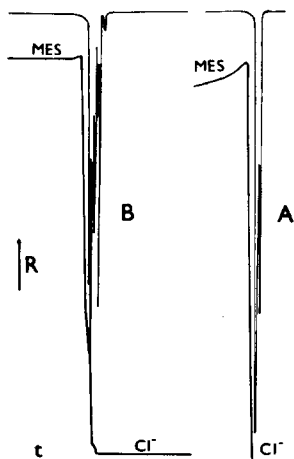


Fig. 4. Isotachopherograms from the conductivity detectors in (A) the pre-separation and (B) the analytical columns obtained in a blank run. Operational system No. 1 (Table I) was used in both columns. The total content of impurities in the system can be deduced from the response in the analytical columns. The driving currents were 200 and 40 μA in the pre-separation and final analytical stages, respectively. R = Increasing resistance; t = increasing time.

pletely eliminated when the mixtures employed for the calibration graph measurements have quantitative compositions close to those of the analysed samples. As the zone lengths of the impurities changed only slightly within the complete series of analyses, the error due to the purification of the solution of the terminating electrolyte²⁶ was also negligible. The influences of the impurities on the reproducibilities of determinations of other constituents were less critical, as the requirements relevant to this performance parameter were at least ten times lower than that for the quantitation of phosphate. Nevertheless, their negative effects could be diminished in the same way as for phosphate.

The isotachopherograms shown in Fig. 5 illustrate the separations of the anionic constituents present in wet-process phosphoric acid. As in the above experiments, phosphate was quantified from the residence time of its zone in the conductivity detector of the pre-separation column (Fig. 5A). The main part of this constituent was removed from the system through a channel connecting the pre-separation column with the leading electrolyte compartment in the bifurcation block^{14,15}. The microconstituents were determined from the detector responses in the analytical column (Fig. 5B). The addition of DCTA to the sample not only was effective for the decomposition of the complexes formed between the sample constituents (see Introduction), but also permitted determinations of Fe^{3+} and Al^{3+} through their anionically migrating chelates. Continuous decompositions of the chelates during the migration^{27,28} could introduce only very small systematic or random errors into the determinations of these cations, as under the analytical conditions employed in this work no free chelating agent due to the chelates decompositions was detected¹³.

The reproducibilities of quantitation currently attainable in the analysis of wet-process phosphoric acid by ITP are shown by the results in Table IV, which were obtained in a series of five analyses of one sample of the acid. The desired sample

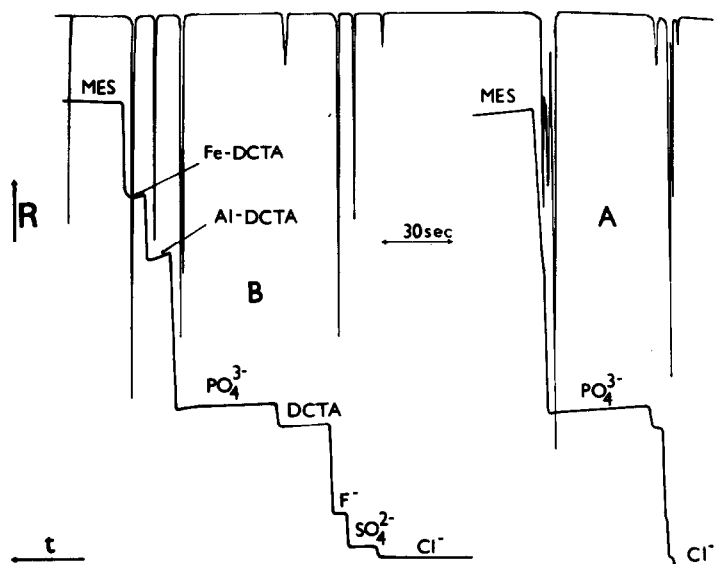


Fig. 5. Isotachopherograms from the analysis of wet-process phosphoric acid in operational system No. 1 (Table I). Phosphate was determined from the zone length in the pre-separation column (A) and the other analytes were determined from their zone lengths in analytical column (B). The main part of phosphate was removed from the analysis after its detection in the pre-separation column. The driving currents were the same as in Fig. 4.

TABLE IV

CHARACTERISTIC REPRODUCIBILITY PARAMETERS OF QUANTITATIVE ITP ANALYSIS OF WET-PROCESS PHOSPHORIC ACID

| Sample constituent | $Z(3)^*$ (sec) | S.D. (sec) | C.V. (%) |
|--------------------|-------------------|---------------|-------------|
| Phosphate | 45.62–61.78 | 0.03–0.15 | 0.04–0.20 |
| Sulphate | 12.80–16.80 | 0.04–0.12 | 0.29–0.90 |
| Fluoride | 6.78– 8.95 | 0.04–0.17 | 0.56–2.22 |
| Al ³⁺ | 10.97–13.65 | 0.06–0.27 | 0.39–2.18 |
| Fe ³⁺ | 8.44–10.92 | 0.04–0.15 | 0.44–1.58 |

* Mean zone length corresponding to different amounts of the sample taken from a stock solution of the acid (for further details, see text).

dilution for each analysis was achieved by weighing required amounts of a stock solution of the acid and water. The stock solutions already contained an excess of DCTA (relative to the contents of Fe³⁺ and Al³⁺) and $5 \cdot 10^{-5}$ M CTABr and its pH was adjusted to 6.0 with ammonia solution. Three ITP runs carried out in each analysis provided a number of experiments that could be treated statistically (characterization by standard deviation and testing for outlying results).

The results of the same analyses were used for the evaluation of contributions of both random and some systematic errors to the quantitation of anionic constituents present in wet-process phosphoric acid (Fig. 6). The errors caused by the pres-

ence of anionic impurities in the operational system can be corrected for as already discussed. For example, the presence of sulphate in the leading and terminating electrolyte solutions (Fig. 4B) explains the positive systematic deviation of the sulphate plot (Fig. 6B), and the positive intercept for fluoride (Fig. 6A) seems explainable only by considering both the presence of impurities in the operational system and sample contamination during handling. Positive intercepts for Fe^{3+} and Al^{3+} (Fig. 6C and D, respectively) can probably be ascribed to contamination of the sample solution from the glassware²⁹. The intercepts in experiments when the glassware was thoroughly cleaned with nitric acid were 3–5 times lower. This cleaning procedure was omitted, however, in the analysis of acid as it could lead to a loss of phosphate

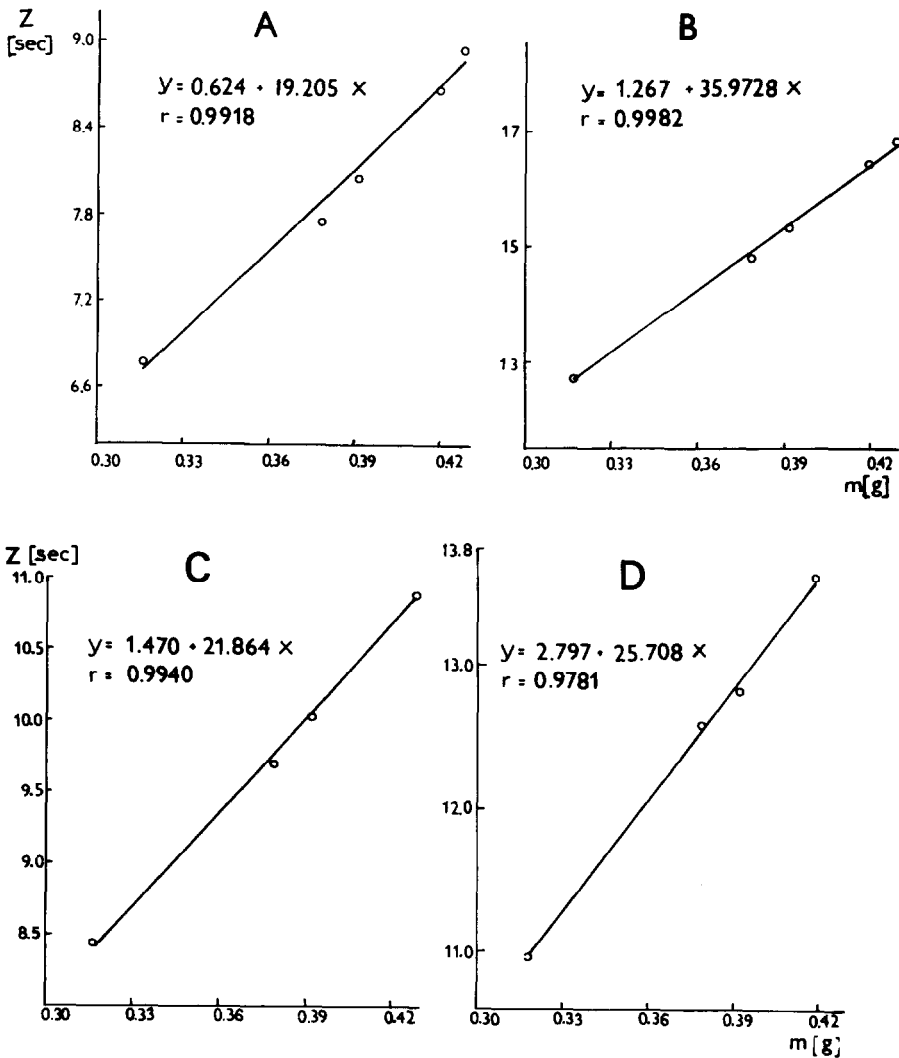


Fig. 6.

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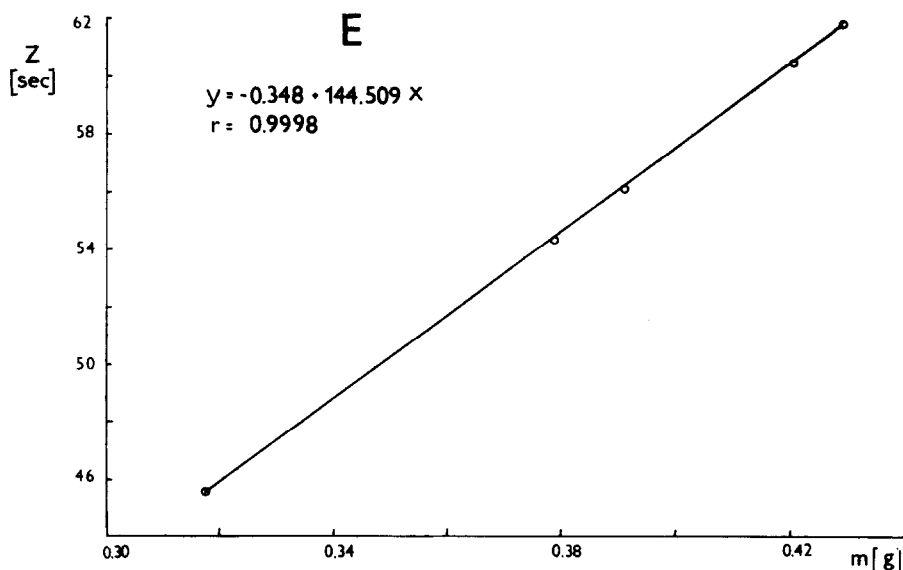


Fig. 6. Comparison of the results of quantitative ITP analyses of constituents present in wet-process phosphoric acid obtained for one sample. m = The amount taken from a stock solution of the acid present in 1 g of the final solution used for the analysis; z = zone length as measured by the stop-watch. A = Fluoride; B = sulphate; C = Fe^{3+} ; D = Al^{3+} ; E = phosphate.

owing to its adsorption on the cleaned surfaces¹. When both the mixtures used for the calibration graph measurements and the samples to be analysed are handled in the same way, these positive errors can obviously be reduced to an acceptable level. Another possibility is to find a treatment procedure that fulfils simultaneously the requirements for the determinations of phosphate and Fe^{3+} and Al^{3+} . A small negative bias in the phosphate plot (Fig. 6E) is equivalent to 0.24% of the response (144.51 sec/g) and it can be ascribed to a loss of analyte during the sample handling rather than to a loss during ITP analysis. Also in this instance analogous conditions for handling the sample and calibration mixtures can reduce this small systematic deviation.

As mentioned above, phosphoric acid contains a precipitate formed by some sample constituents, which needs to be taken into account as the total amounts of constituents are of greatest analytical interest³⁰. Therefore, the precipitate is decomposed by nitric acid. A large excess of nitrate caused problems in its separation from sulphate, thus making reliable quantitation of the latter impossible when using operational system No. 1 (Table I). Our efforts to analyse all constituents in one operational system led to separation conditions requiring undesirable prolongation of the analysis time. Therefore, we divided the determinations for such sample types into two ITP analyses. In one analysis (operational system No. 1) all the anionic constituents with the exception of sulphate were determined, whereas system No. 2 was employed for the determination of this constituent. The isotachopherogram obtained from the detector in the analytical column (Fig. 7) shows a considerable retardation of sulphate in comparison with the separation conditions characteristic of system No. 1 (Fig. 5). This decrease in the effective mobility of sulphate can be

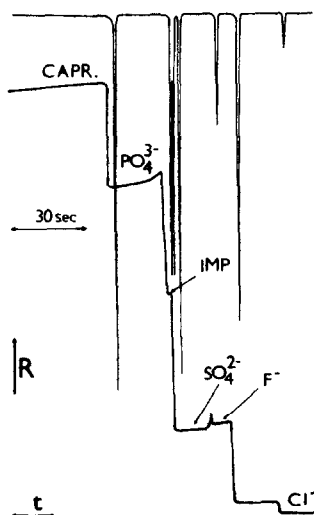


Fig. 7. Isotachopherogram from the determination of sulphate present in phosphoric acid treated with HNO_3 . The analysis was performed in operational system No. 2 (Table I) and only the trace of the recorder from the analytical column is given. The driving currents were 250 and 50 μA for the pre-separation and analytical columns, respectively.

ascribed to a retarding effect of TETA present in the leading electrolyte, and multiply positively charged ionic forms of this co-counter ion influence the effective mobilities of separands through relaxation and electrophoretic effects³¹ and probably also through ion pairing³².

The use of two operational systems for the analysis of wet-process phosphoric acid that needs to be treated with HNO_3 provided reproducibilities of quantitation of the constituents of interest that agreed well with those obtained for acid that could be analysed without any pre-treatment. The prolongation of the analysis time associated with the use of two systems is negligible in comparison with the total analysis time that is typical of the methods reviewed in the Introduction.

CONCLUSIONS

For reasons already given (see Introduction), this work was aimed at a detailed investigation of factors that affect the reproducibilities of ITP determinations of phosphate and other anionic constituents present in wet-process phosphoric acid. The factors that were taken into account can be divided into three relatively independent groups:

(1) Performance of the instrumentation. This includes reproducibility of the sample delivery, elimination of any leaks from the separation compartment, elimination or control of other convective disturbances in the separation compartment, *e.g.*, due to electroosmosis, osmosis and thermal effects, sufficient buffering volume of the channel between the counter-electrode membrane and the separation space, stability of the driving current and reproducibility of zone length measurements.

(2) The use of an optimal operational system. Factors here are resolution of

the constituents to be determined, elimination of undesirable interactions between the sample constituents and minimization of the contents of interfering impurities.

(3) Appropriate sample pre-treatment and sample handling. These include decomposition of the complexes and/or precipitates formed by the constituents to be determined, pH adjustment and elimination of losses of analytes or sample contamination.

Considering these factors, we found in experiments with model mixtures of appropriate compositions and with practical samples that adsorption of phosphate on the walls of the container during sample handling was the most serious source of analytical errors. Adjustment of the pH of the sample solution (to 5.5–6.0) was also necessary to achieve a high reproducibility of the determination of sulphate. The use of DCTA as an additive to the sample was effective for the decomposition of undesirable complexes formed by Fe^{3+} , Al^{3+} , F^- and PO_4^{3-} . It also permitted simultaneous determinations of these cations in the form of anionic chelates.

A large excess of nitrate present in samples treated with HNO_3 (decomposition of precipitate formed by the sample constituents) led us to ITP analysis performed in two operational systems, otherwise a very long analysis time was unavoidable or the determination of sulphate had to be omitted.

As the main reproducibility problems in the determination of phosphate and in determinations of other constituents of interest concerned almost exclusively the third group of factors above and none could be ascribed to the performance of the instrumentation, we feel that ITP is a very promising method for the analysis of ionogenic compounds when a high reproducibility is required (*ca.* 0.1% coefficient of variation).

The results of this work on wet-process phosphoric acid will serve as one of the starting points necessary for a detailed investigation of the accuracy of quantitative ITP analysis of phosphate in this material. Obviously, some of them are of a general validity in instances when ITP needs to be used for a precise analysis or in analyses of these constituents in other materials.

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