ponents may be roughly estimated by comparison with similar mixtures of known composition. In some cases, where each component has some unique absorption without interference from the other, a rough quantitative analysis may be made on the basis of the spectra of pure samples of the components involved.

Mixtures of a solid and a liquid glycol were more difficult to detect. Often the solid did not appear to have dissolved, and so little of it was suspended in the liquid that it probably only scattered light and gave no characteristic absorption of its own. Only the liquid was identified in these cases. In other mixtures, such as that of ethylene glycol and sorbitol, it was sometimes possible to detect a shoulder on the side of a band, indicating the presence of at least one other component mixed with the liquid glycol. However, this was insufficient evidence for complete identification. Probably solvent fractionation means will have to be used to separate solid and liquid glycols, with infrared analysis then being applied to the separate fractions.

Several mixtures of three glycols (in 1 to 1 ratio) were examined. In one case all three were identified (ethylene, diethylene, and triethylene glycols), but as a general rule the evidence is usually inadequate for distinguishing three glycols in a mixture. Unless one of them is particularly unique—e.g., aromatic—and absorbs characteristically without interference from the other two, infrared analysis is not successful in complete identification of most mixtures of more than two polyhydric alcohols.

CONCLUSIONS

Polyhydric alcohols can be readily isolated from unsaturated polyester resins.

The components of the separated alcohol fraction can usually be identified by infrared spectral analysis, using the spectra of dried commercial polyalcohols for comparison.

The infrared method is effective for individual glycols and for mixtures of two liquid glycols, with the components present over a reasonably wide range. Mixtures of a liquid and a solid glycol require further fractionation prior to identification.

The infrared identification of the components of ternary mixtures is only possible in special cases.

ACKNOWLEDGMENT

The contribution of Martha M. Taylor in preparing the illustrative spectra for publication is gratefully acknowledged.

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Identification of Dicarboxylic Acids in Polymeric Esters

Preparation and Properties of Diethyl Esters and Potassium Salts

R. W. STAFFORD, J. F. SHAY[1], and R. J. FRANCEL

American Cyanamid Co., Stamford, Conn.

The diethyl esters of eight selected dicarboxylic acids were prepared and purified. Various physical properties were determined on the purified products; the potential applicability of these properties to the analysis of mixtures of esters was evaluated. The resolution of mixtures was found possible by the application of distillation and/or ultraviolet and infrared spectroscopy. The dipotassium salts were prepared from the diethyl esters, and the Kappelmeier procedure was evaluated in the process. As characteristic derivatives, the salts were found to be less applicable to the identification of the acids than were the esters.

The increasing variety of acidic components used in the formulation of polymeric esters has introduced analytical complications which seriously qualify the previously reliable procedures used in the investigation of these commercially important resins. In recognition of the need for modified and/or new analytical procedures for this purpose, a series of investigations was carried out in this laboratory.

Attention was concentrated on the dicarboxylic acids, as represented by eight commercially important compounds. As the initial result of this work, a method employing the infrared spectra of the *N*-benzylamides was proposed (*16*) for the identification of these acids as they occurred in commercial polyesters; the method was based on data obtained during one phase of the broader investigation. In the present paper, data derived from alternative lines of study, performed concurrently on the same eight acids, are reported and discussed.

Originating in 1935, the first reported methods (*3*, *5*, *8*, *9*, *11*) for the analysis of alkyd resins were naturally aimed at the determination of phthalic acid. Perhaps the simplest and most reliable of these earlier procedures is that devised by Kappelmeier who subsequently discussed his technique, perfected for the resins commercially available at the time, in some detail (*10*). The method is based on the quantitative precipitation, under controlled conditions, of dipotassium phthalate monoalcoholate during saponification of the polyester with potassium hydroxide dissolved in absolute alcohol. Although primarily

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[1] Present address, Fortier Plant, American Cyanamid Co., Avondale, La.

designed to effect the quantitative estimation of phthalic acid, this procedure possesses the additional advantage that in separating the alcohol-insoluble salt from the soluble monocarboxylic acid salts and other modifiers, it also permits the quantitative separation and estimation of the latter. As a quantitative method for phthalic acid the procedure, in modified form, comprises the American Society for Testing Materials (*1*) (ASTM) standard method of test.

The Kappelmeier procedure suffers from the disadvantage, recognized in the ASTM directions, that the salts of many other dicarboxylic acids are completely or partially insoluble in absolute ethanol under the experimental conditions. As the variety of polycarboxylic acids used in polyester formulation increased, this interference assumed serious proportions. Stafford and Williams (*17*) have suggested a qualitative optical method for the resolution of the Kappelmeier salts of simple mixtures of acids.

In more recent attempts to broaden the scope of the procedure, Swann (*20*) has proposed a method, primarily chemical in nature, which is designed to permit the quantitative estimation of a number of pertinent dicarboxylic acids. Shreve and Heether (*15*) have suggested that the percentage of phthalic acid present in a polyester can be determined by the analysis of the ultraviolet spectrum of the mixture of acids separated as salts by the saponification procedure. The quantitative detection is based on the absorption maximum occurring at 2760 A., and the spectrum of potassium acid phthalate is used as standard. Interferences at this wave length by other aromatic acids and by maleic and fumaric acids are taken into consideration. Both of these approaches, as applied to phthalic acid, have been subjected to collaborative testing by ASTM Subcommittee XI, Committee D-1, and have been accepted by the society as tentative revisions for the standard method (*1*).

Investigators in allied fields have reported on techniques potentially applicable to the current problem. According to Mathews, Warren, and Michel (*14*), their previously reported work on the identification of acids by the x-ray powder diffraction patterns of the corresponding anilides has been extended to include the silver salts and the amides, with the salts preferred because of pattern differentiation and ease of presentation. Castle (*4*) has used the correlation between the index of refraction and the melting point to estimate the probable composition in a homologous series such as that represented by the oxalic-sebacic group of saturated dibasic acids. Marvel has suggested the separation of polybasic acids by fractional extraction (*13*) and partition chromatography (*12*).

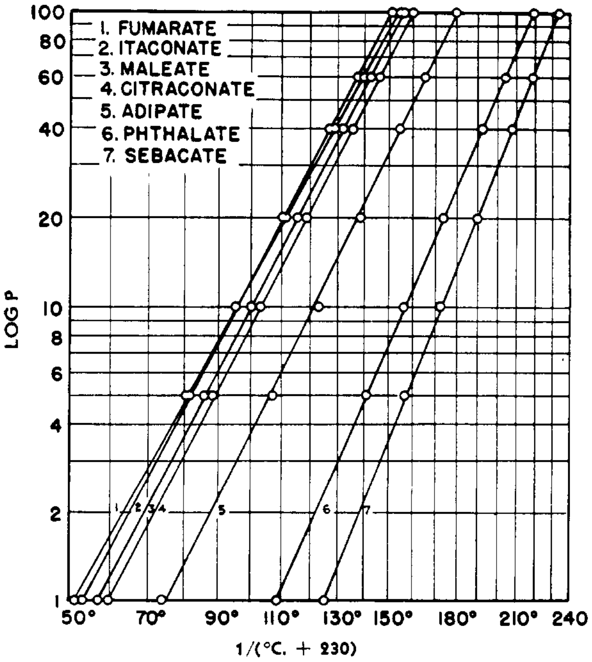
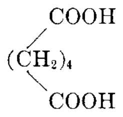


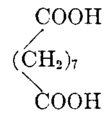
Figure 1. Plot of Stull Vapor Pressure Data

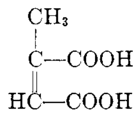
Stark, Goodban, and Owens (*18*) have reported on the chromatographic separation of a number of dicarboxylic acids on ascending columns. Most recently, Higuchi, Hill, and Corcoran (*6*), working on the chromatographic separation of the C_4—C_{10} dicarboxylic acids, resolve mixtures of the saturated, straight-chain acids on a partition column using pH 5.4 citrate buffer as the internal phase for the separation of acids above adipic, and water for the separation of acids below adipic.

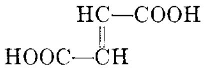
PREPARATION AND PROPERTIES OF DIETHYL ESTERS

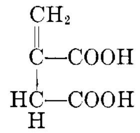
As in the earlier study (*16*), eight acids were chosen:

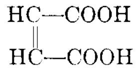

Adipic

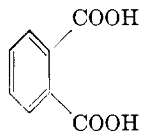

Azelaic

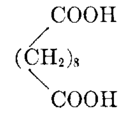

Citraconic


Fumaric


Itaconic


Maleic


Phthalic


Sebacic

Approximately 1 kg. of the diethyl ester of each of the above acids was prepared and then purified by vacuum fractionation. The usual physical properties were determined on the fractionated esters and are reported together with presumably more accurate comparative data from the literature. The purpose of this itemized treatment is to illustrate the extent to which this set of compounds qualifies as standards for the direct application of infrared and ultraviolet spectral representation and for the evaluation of the Kappelmeier procedure, and as parent compounds for the preparation of derivatives such as the salts and the *N*-benzylamides.

Table I. Vapor Pressure Data of Esters at 50 Mm.

Ester	Temperature, ° C.	
	Observed	Corrected[a]
Fumarate	129.5	131
Itaconate	133.5	137
Maleate	135	139
Citraconate	139.5	143.5
Adipate	156.5	161.5
Azelate	183	189.5
Phthalate	192	200
Sebacate	205	213.5

[a] Corrected to nearest 0.5° for emergent stem.

Preparation. A Fischer-type esterification, using the azeotropic method of Young (*21*) was employed. The reactions were carried out in a 3-liter single-necked flask containing Berl saddles to prevent bumping, and equipped with a 28-inch jacketed column of 1-inch diameter, packed with Berl saddles. The column was connected to a Dean-Stark moisture distillation trap of 50-ml. capacity, fitted with a draining stopcock and a water-cooled condenser.

The technical grade acids used were recrystallized once from water. To an amount of acid calculated to yield approximately 1 kg. of the diethyl ester were added a 100% molar excess of ethanol, 300 ml. of benzene, and 10 grams of toluenesulfonic acid monohydrate as catalyst. Removal of the water of condensation required 20 to 30 hours. The column was then heated, and the excess ethanol and benzene were stripped off to give a yield of crude ester in excess of 95% in each case. Since the crude esters were practically neutral, with determined acid values of 5 or less, it was not considered necessary to preface distillation with an alkaline wash.

Distillation Procedure and Data. Distillation was carried out in a vacuum fractionation apparatus of conventional design. The apparatus was balanced under total reflux until equilibrium had been reached, and the constant-boiling distillate was removed at 50-mm. pressure. The azelate and sebacate esters foamed so strongly at 50 mm. that after recording the data at this pressure, it was necessary to distill the bulk of these esters at 15 mm. The vapor pressure data are listed in Table I.

Diethyl itaconate polymerized during vacuum distillation, resulting in a reduced yield of monomeric ester. The yields of the other once-distilled esters were in excess of 90%.

From the data collected by Stull (*19*), which were published subsequent to the above experiments, the data in Table II were taken for comparison. No data were listed for diethyl azelate. The data (Table II) were plotted on a Cox chart to give the curves reproduced in Figure 1. The vapor pressures at 50 mm. were taken from the curves for comparison with those determined on the esters. The results are listed in Table III.

Table II. Literature Vapor Pressure Data at Reduced Pressures

Ester	Temperature, ° C. 1 mm.	5 mm.	10 mm.	20 mm.	40 mm.	60 mm.	100 mm.
Fumarate	53.2	81.2	95.3	110.2	126.7	137.7	151.1
Itaconate	51.3	80.2	95.2	111.0	128.2	139.9	154.3
Maleate	57.3	85.6	100.0	115.3	131.8	142.4	156.0
Citraconate	59.8	88.3	103.0	118.2	135.7	146.2	160.0
Adipate	74.0	106.6	123.0	138.3	154.6	165.8	179.0
Phthalate	108.8	140.7	156.0	173.6	192.1	204.1	219.5
Sebacate	125.3	156.2	172.1	189.8	207.5	218.4	234.4

Table III. Determined *vs.* Calculated Vapor Pressure Data at 50-Mm. Pressure

Ester	Temperature, ° C. Determined	Calculated
Fumarate	131	132.5
Itaconate	137	135
Maleate	139	137.5
Citraconate	143.5	141.5
Adipate	161.5	160.5
Azelate	189.5	Not listed
Phthalate	200	199
Sebacate	213.5	214.5

Saponification Results. Before saponification values were determined, the esters were redistilled at 25 mm., and the refractive indices before and after distillation were found to agree. The itaconate and citraconate esters were not redistilled because of the partial polymerization of the former during the first fractionation. Preliminary acid value determinations indicated that the twice-distilled esters were neutral to a phenolphthalein end point, whereas the once-distilled itaconate and citraconate showed some slight acidity. This was removed by passing the esters through a column packed with three layers of absorbent, comprising a bottom layer of Hi-Flow Super-Cel diatomaceous earth (Johns-Manville Co.), a middle layer of an aqueous paste of sodium bicarbonate plus the Hi-Flow absorbent, and a top layer of the Hi-Flow absorbent. Two passes through the column yielded neutral esters, the infrared spectra of which showed the presence of 1 to 2% water. The latter was removed by drying in a vacuum desiccator over calcium hydride.

Samples comprising 1.5 to 2.5 grams of neutral ester were weighed into 250-ml. flasks from a Lunge pipet, and 10 ml. of benzene were added to each flask. Alcoholic potassium hydroxide (about 0.5*N*) was next added in at least 100% excess over the amount theoretically required to saponify the ester. A pair of blanks were run in each experiment. The solutions were refluxed under air condensers for 2 hours on a water bath. After washing down the apparatus and cooling, the solutions were back-titrated to a phenolphthalein end point with 0.5*N* hydrochloric acid run in from a 100-ml. buret calibrated by the National Bureau of Standards. The results are listed in Table IV.

Table IV. Saponification Values of Prepared Esters

Ester	Determined	Average[a]	Theory
Fumarate	652.5 652.2	652	652.3
Maleate	652.3 651.4	652	652.3
Citraconate	603.5 602.7	603	603.2
Itaconate	602.7 603.2	603	603.2
Adipate	554.5 555.3	555	555
Phthalate	505.3 504.5	505	505.4
Azelate	457.0 456.4	457	459.8
Sebacate	433.2 433.4	433	434.9

[a] Averaged to nearest integer; results reproducible to nearest ±1.

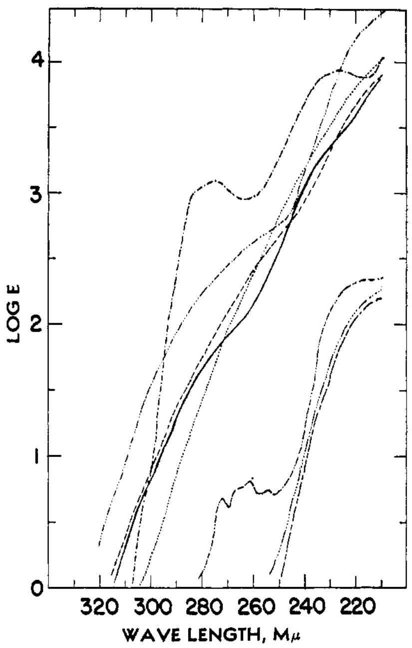


Figure 2. Ultraviolet Absorption Spectra of Diethyl Esters

.— Phthalic
...— Fumaric
.... Citraconic
— — Maleic
——— Itaconic
..—— Azelaic
.....— Sebacic
— —— Adipic

Other Physical Properties. Refractive Indices and Densities of the esters were determined at 20° ± 0.05°, using an Abbe refractometer for the former and a 5-ml. pycnometer for the latter. Comparative data were taken from Huntress and Mulliken (*7*). The results are listed in Table V.

Ultraviolet Spectra of the esters are reproduced in Figure 2. The data on which the plots are based were obtained by use of a Beckman quartz photoelectric spectrophotometer, Model

Table V. Refractive Indices and Densities of Esters.

Ester	Refractive Indices, n_{20}^{D} Determined	Reported	Densities, d^{20} Determined	Reported
Adipate	1.4275	1.42765	1.007	1.0090
Azelate	1.4351	1.43509	0.972	0.97294
Citraconate	1.4449	1.4442	1.048	1.0491
Fumarate	1.4408	1.44103[a]	1.052	1.05189[b]
Itaconate	1.4408	1.4377	1.045	1.0467
Maleate	1.4413	1.44156[c]	1.064	1.06740
Phthalate	1.5019	1.5019	1.119	1.1175
Sebacate	1.4368	1.43657	0.963	0.9631

[a] 20.1° C.
[b] 20.6° C.
[c] 19.9° C.

DUV, equipped with a Nester water-cooled hydrogen lamp. Fused quartz absorption cells of 5- and 10-mm. light path length were used, as well as adjustable Hilger micrometer Baly cells, variable from 5.00 to 0.01 mm. in length. Redistilled 95% ethanol was employed as solvent as used in the comparison or blank cells.

Beer's law was used in the form:

$$\log P_0/P = A = abc = \frac{\epsilon}{M} bc$$

where P_0 and P are the intensities of the incident and transmitted light, respectively. A is the absorbance (optical density), a is the absorptivity (specific extinction), ϵ is the molar absorptivity (molar extinction), M is the molecular (formula) weight, b is the cell light path length in millimeters, and c is the concentration in grams per 100 ml. The spectra are plotted as the common logarithm of the molar absorptivity *vs.* wave length in Angstroms, which procedure keeps the curve shape independent of concentration.

INFRARED SPECTRA of the esters are reproduced in Figures 3 to 5. The spectra shown were obtained on the esters contained in a cell of 0.01-mm. thickness, using a Perkin-Elmer infrared spectrometer Model 12A. The instrument was equipped with a sodium chloride prism and had been converted to a percentage transmittance spectrophotometer. To conserve space, only the region from 1800 to 700 cm.$^{-1}$ is shown.

DISCUSSION OF EXPERIMENTAL RESULTS

The distillation data led to four conclusions:

Within the limitations of the method, the prepared esters appeared to be sufficiently pure to serve as standards.

The vapor pressures of the unsaturated esters are not sufficiently separated to permit fractionation with the usual laboratory apparatus.

There is sufficient difference between the vapor pressure of the citraconate and the adipate to permit the separation of the unsaturated esters as a group from the saturated esters as a group, assuming 50 to 100 ml. are available for a Podbielniak distillation.

There is sufficient separation among the vapor pressures of the esters of the saturated group to permit further fractionation, assuming each ester is present in an amount exceeding the hold-up of the column employed.

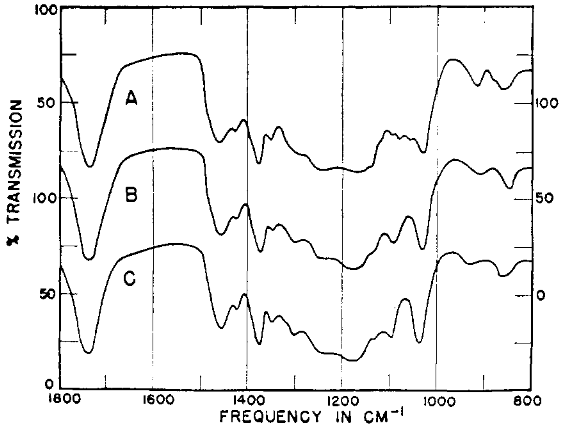


Figure 3. Infrared Spectra of Esters

A. Diethyl adipate
B. Diethyl azelate
C. Diethyl sebacate

The saponification data confirmed the indication of purity by the inherently less accurate and precise distillation data.

The refractive index and density data supplied further confirmation of purity. The high refractive index of the itaconate ester is probably caused by the presence of polymer. Beilstein has pointed out (*2*) that this ester polymerizes during distillation and that this polymerization is characteristic of the pure ester. Since Beilstein reports $n_{20}^{D} = 1.48933$ for the polymer, as little as 5% would be sufficient to cause the increase observed. It is possible that the slightly high value for the citraconate may be similarly explained.

In the ultraviolet spectra both the wave-length positions and intensities fell in the regions expected from the chromophoric groupings of the compounds. This, plus the virtual absence of absorption in the weakly absorbing compounds, furnished additional proof of purity except for a discrepancy noted below. In Figure 2, the curve of the phthalate ester is noticeably different from the others, with a definite maximum near 2750 A. This band is attributed to an electronic transition related to the phenomenon which gives rise to the familar absorption spectrum of benzene—that is, it is associated with the benzene ring.

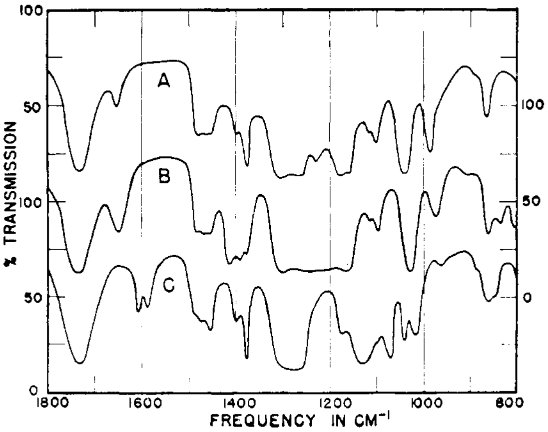


Figure 4. Infrared Spectra of Esters

A. Diethyl fumarate
B. Diethyl maleate
C. Diethyl phthalate

The strong absorption shown by the fumarate, maleate, itaconate, and citraconate esters is attributed to the conjugated carbon and oxygen systems present. The spectra of the maleate and the citraconate esters are, as expected, very similar, since the two structures differ only by a methyl group. The increased intensity of the fumarate spectrum is attributed to the trans configuration as compared to the cis. The close resemblance between the citraconate and itaconate spectra seems surprising, for the itaconate might be expected to absorb at shorter wave lengths because of the shorter formal conjugated resonating system present. This similarity may be due to geometrical effects.

The spectra of the adipate, azelate, and sebacate esters show the expected weak absorption at short wave lengths, because of the lack of conjugation. The series of sharp bands in the azelate spectrum is due to the presence of a small amount of impurity. The concentration of this impurity may be estimated from the band intensities as 0.08% if an aromatic or 0.02% if a triconjugated double bond fatty acid.

The infrared spectrum of each of the esters exhibits the characteristic ester carbonyl absorption at about 1735 cm.$^{-1}$. The absorption at about 1645 cm.$^{-1}$ in the unsaturated esters is associated with the C=C group. The spectrum of diethyl phthalate includes in addition the characteristic absorption of an ortho disubstituted phenyl ring, including bands at 1600, 1580, and 745 cm.$^{-1}$.

Although the spectra of the azelate and the sebacate show such minor differences that it would be difficult to distinguish between these esters when present in mixtures, the spectra of the esters in general are otherwise distinctive, and could be used for identification purposes even in mixtures containing as many as three of these esters. This characteristic absorption can be used to advantage by prefacing the spectral analysis with a fractional distillation of a given mixture to separate the lower boiling unsaturated group from the higher boiling saturated group. Since the presence of more than two acids from each group would be a rare occurrence in a commercial polyester, spectral analysis of the low and high boiling fractions should permit the identification of the components, respectively, therein.

PREPARATION AND PROPERTIES OF DIPOTASSIUM SALTS

Preparation. The Kappelmeier procedure, comprising the saponification of a dicarboxylic acid ester with an approximately 0.5*N* solution of potassium hydroxide in absolute alcohol under such conditions that the dibasic acid separates as an insoluble salt, was designed for the quantitative estimation of phthalic acid. Since experience has demonstrated that many other dicarboxylic acids yield insoluble potassium salts under the conditions of the experiment, the preparation of the salts was also utilized as a means of investigating the quantitative aspects of the reaction.

Evaluation of Kappelmeier Procedure. As now recommended, the salient features of the Kappelmeier procedure are itemized by the American Society for Testing Materials (*1*). This was followed precisely on the eight esters under investigation. The quantitative data on duplicate experiments are listed and compared with theory in Table VI.

Table VI. Determination of Acid

Ester	Salt, %	Average	Factor	Acid, %	Theory	Detd./ Theory
Fumarate	111.18 111.56	111.37	0.6042	67.29	67.44	99.79
Maleate	124.52 125.84	125.18	0.6042	75.63	67.44	112.14
Citraconate	Indeterminate	...	0.6311	...	69.89	...
Itaconate	Indeterminate	...	0.6311	...	69.89	...
Adipate	112.41 113.52	112.97	0.6577	74.32	72.28	102.8
Phthalate	130.83 131.06	130.95	0.5764[a]	75.48	74.77	100.9
Azelate	Indeterminate	...	0.7121	...	77.05	...
Sebacate	109.45 109.67	109.56	0.7266	79.61	78.29	101.69
Maleic acid	166.37 166.25	166.31	0.6042	100.48	100.00	100.48

[a] Based on monoalcoholate.

Infrared Spectra of Potassium Salts. The various potassium salts, obtained as described above, were examined by infrared spectral methods, using the instrumentation previously described. In this instance, the samples, being solids, were examined in the form of Nujol mulls. As gravimetric reproducibility in the preparation of the salts was not obtained in all cases, and, even when obtained, yielded anomalous data in one instance, it was decided that these salts could not be generally considered as standards for comparison. Reproductions of the spectra are hence omitted at this time.

DISCUSSION OF EXPERIMENTAL RESULTS

The ASTM data led to several conclusions:

The method is satisfactory as now constituted for phthalate, fumarate, sebacate, and adipate, although it was necessary to dry the adipate salt for an additional 4 hours to bring it to constant weight.

The maleate consistently yielded a high result.

The citraconate and itaconate salts were characterized by marked postprecipitation during filtration; the data were hence not quantitative. The salts obtained were sufficiently well crystallized, however, to permit fairly rapid filtration and washing. This suggested that quantitative results may be possible if the procedure were modified.

The azelate was gelatinous and almost impossible to filter. It separated only after the addition of the ether to the saponification solution.

In view of the results, it is apparent that the ASTM method (*1*) is not generally applicable as a quantitative procedure, although it may be so used with certain combinations of acids that have been identified prior to attempting quantitative work.

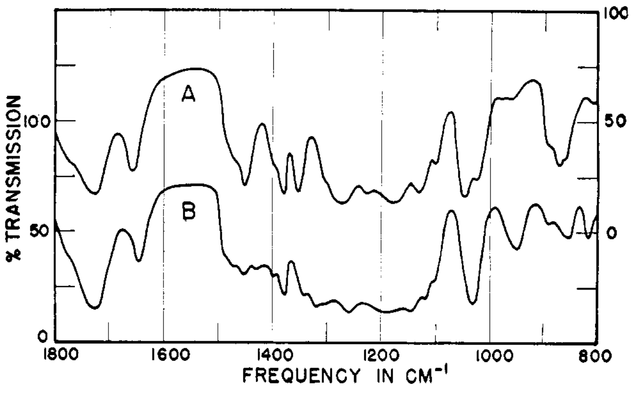


Figure 5. Infrared Spectra of Esters

A. Diethyl citraconate
B. Diethyl itaconate

The maleate salt, being apparently unique, was investigated further in an attempt to account for the consistently high results obtained. With the exception of the phthalate, which is known to crystallize with one molecule of ethanol per molecule of dipotassium salt, the factors for the conversion of percentage salt to percentage acid were calculated on the basis of the ethanol-free salt. When so calculated, the maleate yielded results about 112% of theory. If potassium maleate crystallized with one molecule of ethanol, the determined percentage acid, calculated with the factor used above, would represent 123.95% of theory. If it were the hemi alcoholate which crystallized, the determined percentage acid would be 111.98% of theory, compared with 112.14% found.

To check this indication, the infrared spectrum of a mull of the maleate salt in perfluokerosene was analyzed. In addition to the expected bands, CH_3, CH_2, and OH absorptions were observed. It is strongly suggested that dipotassium maleate, as prepared from the diethyl ester, contains alcohol of crystallization. This indication was interesting, in view of the fact that the salt prepared directly from maleic acid under the same experimental conditions was in good agreement with theory, and showed no evidence of ethanol in its infrared spectrum. It would therefore appear that the presence of ethanol of crystallization requires the ethyl ester as the starting compound.

Analysis of the infrared spectra of the salts led to the following conclusions:

The various spectra were sufficiently characteristic to permit identification of the individual acids.

Most pairs of salts could be readily identified. Exceptions to this were itaconate plus citraconate, and azelate plus any of the others.

Mixtures including three or more components could be identified only with the greatest difficulty.

In addition to the phthalate and maleate, the itaconate and citraconate salts both apparently contained alcohol of crystallization, judging from the strong hydroxyl absorption evident in their spectra. A method for the quantitative separation of these salts will have to be devised before this indication can be investigated further.

The azelate showed a paucity of characteristic bands.

CONCLUSIONS

Both the diethyl esters and the dipotassium salts are characteristic derivatives which permit the identification of individual dicarboxylic acids. The infrared and/or ultraviolet spectra are the most determinative properties of these derivatives.

When mixtures of acids are involved, the esters permit more effective resolution than do the salts. Neither derivative is as determinative as is the *N*-benzylamide, the application of which has been reported (*16*).

The Kappelmeier procedure for phthalic acid, as represented by the ASTM standard method (*1*), is not generally applicable as a quantitative method, although it may be so used with certain combinations of acids which have been identified prior to attempting quantitative work.

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Determination of Triphosphate and Pyrophosphate by Isotope Dilution

O. T. QUIMBY, A. J. MABIS, and H. W. LAMPE

Miami Valley Laboratories, Procter & Gamble Co., Cincinnati 31, Ohio

Prior to the present study there has been no solution method capable of determining total triphosphate in the presence of ortho-, pyro-, and trimetaphosphates. Since tracer studies have shown that either triphosphate as $Na_5P_3O_{10}$ or pyrophosphate as $Na_4P_2O_7$ can be adequately purified by three to five crystallizations from water–ethyl alcohol mixtures at room temperatures, both tri- and pyrophosphates can be determined by isotope dilution. No systematic bias is detected in the analysis for pyrophosphate. That observed for triphosphate did not exceed +2% absolute and can be made negligible by suitable correction. Based on replicate determinations the standard deviation is 1.5% absolute for $Na_5P_3O_{10}$ and 1.0% absolute for $Na_4P_2O_7$. The time required for each determination on a sample is 2 to 4 man-hours. The time elapsing before the result becomes available is 1 to 3 days. Since inorganic salts—e.g., sulfate and silicate—and anionic detergents do not interfere with the purification of tri- or of pyrophosphate, the method is applicable to triphosphated detergents as well as to commercial triphosphate.

SOLUTION methods available for the determination of sodium triphosphate and sodium pyrophosphate in mixtures of the two involve precipitation of the two phosphate ions by zinc (*1-3*, *8*). In case A (*1-3*) the conditions are arranged so that pyrophosphate is determined by precipitation and triphosphate by titration of released acidity, after correction for the acidity released by pyrophosphate. In case B (*8*) conditions are adjusted so that both pyro- and triphosphate precipitate quantitatively (the latter as $NaZn_2P_3O_{10}$). Analysis of the precipitate for zinc and phosphorus allows calculation of the pyro- and triphosphate content, provided that no other phosphate species are present in the precipitate. Both methods are therefore indirect and, in addition, suffer interferences if higher polyphosphates are present. Thus, in A higher polyphosphates contribute to the titration and in B some of the higher polyphosphates precipitate, especially those just above triphosphate (*10*).

The x-ray method reported recently (*5*) is specific for these species, but requires the sample to be in solid form; it will give the total tri- or pyrophosphate only when both species are present wholly in crystalline form. Furthermore, interference results from the presence of any crystalline ingredient with diffraction lines at the same position as those phosphate lines used for analysis.

Thus, there is a need for a method which is specific for the individual phosphate (pyro- or tri-), which suffers no interference from other soluble phosphates, and which gives the total amount of each species, regardless of physical state of the sample. The present method meets these requirements, and, in addition, suffers no difficulties if sodium sulfate, sodium silicate, and anionic detergents are also present. It is therefore applicable to commercial detergents containing pyro- and triphosphate as well as to commercial sodium tripolyphosphate.

PRINCIPLE OF METHOD

Since the isotope dilution technique does not require full recovery of the species being determined, but merely isolation of some of that species in essentially pure form, ordinary fractional recrystallization procedures found effective in purifying sodium tri- and pyrophosphates have been used for said isolation. To avoid heating or lengthy evaporations, the phosphate species is recovered from a fairly concentrated aqueous solution by adding ethanol to induce precipitation at 25° to 35° C.

To express the principle of the method in quantitative terms, imagine that a mg. of tagged triphosphate of specific activity, S_o, is diluted by b mg. of inactive triphosphate in the sample to be analyzed for sodium triphosphate. The specific activity, S, of the pure triphosphate isolated from the mixture is related to the other quantities by the equation:

$$b = a(S_o/S - 1) = a(Z - 1) \qquad (1)$$