

The Analysis of Mixtures of the Hydrochlorides of Hexamethylenediamine, *p*-Diaminodicyclohexylmethane and ϵ -Aminocaproic Acid

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The method developed for the chromatographic separation and determination of mixtures of the hydrochlorides of hexamethylenediamine, *p*-diaminodicyclohexylmethane and ϵ -aminocaproic acid involves the separation of a mixture of *p*-diaminodicyclohexylmethane dihydrochloride and ϵ -aminocaproic acid hydrochloride on a cellulose column, with *sec*.-butanol - formic acid - water as eluting solvent. Hexamethylenediamine dihydrochloride is subsequently eluted from the column with an alcohol - water solvent.

The proportions of the respective hydrochlorides are determined by analysis of the two eluates after evaporation to dryness, and allowance is made for changes that take place in the composition of the individual hydrochlorides on passage through the column.

In a previous paper¹ attention was drawn to the chromatographic separation of the hydrochlorides of ϵ -aminocaproic acid, hexamethylenediamine and *p*-diaminodicyclohexylmethane. Experiments on cellulose columns had indicated that it was possible to separate hexamethylenediamine dihydrochloride from the other two hydrochlorides, but no quantitative work had been carried out on the system. It seemed desirable to carry out such work, because if successful it would permit satisfactory conclusions to be drawn about the composition of interpolymers of nylon 6, nylon 66 and nylon PACM 6.

EXPERIMENTAL

Preliminary tests were carried out, as a result of which a procedure based on the following considerations was worked out.

An aqueous alcoholic solution of the three hydrochlorides was applied to a cellulose column and then eluted with a solvent mixture containing definite proportions of *sec*.-butanol, formic acid and water. After passage of a known volume of this solvent through the column, the eluate was evaporated to dryness, and a determination of total acidity and total chlorine

was carried out on the residue obtained. From these determinations the proportions of ϵ -aminocaproic acid hydrochloride and *p*-diaminodicyclohexylmethane dihydrochloride in this eluate were calculated. The hexamethylenediamine dihydrochloride in the column was then eluted with an alcohol-water solvent of definite composition and the eluate was subsequently evaporated to dryness. Determination of chloride in this residue gave a measure of the hexamethylenediamine dihydrochloride in this portion of the eluate.

When this test was applied to mixtures of (a) ϵ -aminocaproic acid hydrochloride and hexamethylenediamine dihydrochloride, (b) *p*-diaminodicyclohexylmethane dihydrochloride and hexamethylenediamine dihydrochloride, and (c) ϵ -aminocaproic acid hydrochloride, *p*-diaminodicyclohexylmethane dihydrochloride and hexamethylenediamine dihydrochloride, the results shown in Table I were obtained.

TABLE I

CHROMATOGRAPHIC SEPARATION OF MIXTURES OF THE BASE HYDROCHLORIDES,
FOLLOWED BY THEIR VOLUMETRIC DETERMINATION

	Mixture of ϵ -aminocaproic acid hydro- chloride and hexamethylene- diamine dihydrochloride		Mixture of <i>p</i> -diaminodicyclo- hexylmethane di- hydrochloride and hexamethylene- diamine dihydrochloride		Mixture of ϵ -amino- caproic acid hydrochloride, <i>p</i> -diaminodicyclo- hexylmethane di- hydrochloride and hexamethylene- diamine dihydrochloride	
	Added, g	Found, g	Added, g	Found, g	Added, g	Found, g
ϵ -Aminocaproic acid hydrochloride	0.0928	0.0878	—	—	0.1012	0.0963
<i>p</i> -Diaminodicyclohexylmethane di- hydrochloride	—	—	0.1000	0.0973	0.0516	0.0497
Hexamethylenediamine dihydro- chloride	0.1063	0.0974	0.1000	0.0965	0.0499	0.0480

It will be seen that all the recoveries were low, but in general the recovered substances are present in proportions that closely approximate to those in the original mixtures.

In a second set of experiments on two component mixtures of known composition the material recovered in each fraction from the column was weighed. This material was then redissolved and titrated by the procedure outlined above. The results obtained are shown in Table II.

TABLE II

CHROMATOGRAPHIC SEPARATION OF MIXTURES OF THE BASE HYDROCHLORIDES,
FOLLOWED BY THEIR GRAVIMETRIC AND VOLUMETRIC DETERMINATION

	Mixture of ϵ -aminocaproic acid hydrochloride and hexamethylenediamine dihydrochloride			Mixture of <i>p</i> -diamino- dicyclohexylmethane dihydrochloride and hexamethylenediamine dihydrochloride		
	Added, g	Found by weight, g	Found by titration, g	Added, g	Found by weight, g	Found by titration, g
ϵ -Aminocaproic acid hydrochloride	0.0488	0.0496	0.0450	—	—	—
<i>p</i> -Diaminodicyclohexylmethane di- hydrochloride	—	—	—	0.0938	0.0904	0.0900
Hexamethylenediamine dihydro- chloride	0.1489	0.1456	0.1357	0.1060	0.1079	0.0999

It will be noted from these results that the amounts found by weighing the evaporated eluates were in quite good agreement with the amounts of the respective hydrochlorides added. Nevertheless, the figures obtained by titration of the evaporated eluates did not agree with their weights, *i.e.*, there was evidence that some change had taken place in the composition of the respective hydrochlorides either on the column or on evaporation of the eluates.

In order to examine this point in greater detail, experiments were carried out on hexamethylenediamine dihydrochloride alone.

A known weight of the material was submitted to the chromatographic test, with the results shown in Table III.

TABLE III

GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF HEXAMETHYLENEDIAMINE DIHYDROCHLORIDE AFTER PASSING THROUGH A CHROMATOGRAPHIC COLUMN

			Hexamethylenediamine dihydrochloride		
			Added, g	Found by weight, g	Found by titration, g
Column 1	0.2084	0.2047	0.1969
Column 2	0.2105	0.2075	0.2010
Column 3	0.2108	0.2087	0.2025
Column 4	0.2024	0.1999	0.1943

The infra-red spectrum of the material recovered from the eluate was then compared with the spectrum of the original hexamethylenediamine dihydrochloride. These spectra are given in Fig. 1.

Although the spectra are very similar, the material from the eluate shows increased absorption at about 1620 cm^{-1} , which is evidence of the presence of a constituent containing a carbonyl grouping.

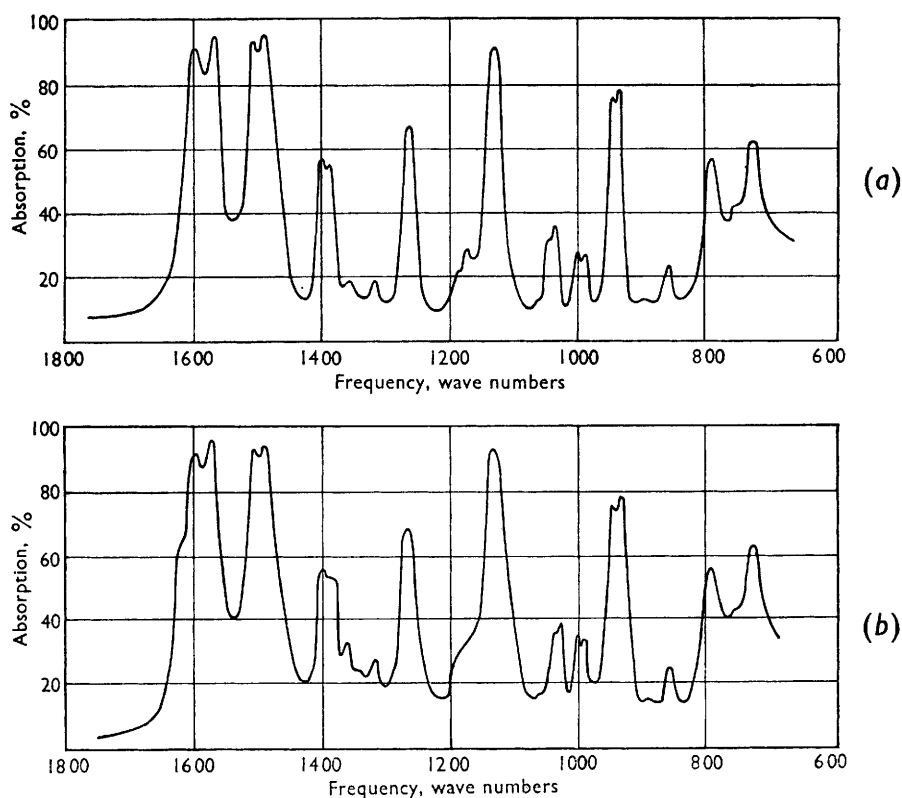


Fig. 1. Infra-red spectra of: (a) hexamethylenediamine dihydrochloride; (b) hexamethylenediamine dihydrochloride that has been eluted from the chromatographic column. The spectra were prepared by the potassium bromide disc method; 1 per cent. of substance in potassium bromide; thickness of disc 1 mm

Since formic acid is used in the eluting solvent, it was suspected at this stage that the material from the column might be contaminated with either the diformyl or the dihydroformate derivative of hexamethylenediamine.

These derivatives were prepared by the following procedures—

Hexamethylenediamine diformyl—Hexamethylenediamine was heated under reflux with 90 per cent. formic acid and then taken to dryness; the residue was recrystallised from ethanol. This material was found to have the following composition on analysis—

Carbon	= 55.9 per cent.	(theoretical value 55.7 per cent.)
Hydrogen	= 9.2 per cent.	(theoretical value 9.4 per cent.)
Oxygen	= 18.8 per cent.	(theoretical value 18.6 per cent.)
Nitrogen	= 16.6 per cent.	(theoretical value 16.3 per cent.)

The infra-red spectrum of this material is shown in Fig. 2.

Hexamethylenediamine dihydroformate—Hexamethylenediamine was neutralised with 90 per cent. formic acid in ethanol solution. Acetone was added to the solution and the precipitate obtained was filtered off and washed with acetone. This material was found to have the following composition on analysis—

Carbon	= 45.9 per cent.	(theoretical value 46.0 per cent.)
Hydrogen	= 9.9 per cent.	(theoretical value 9.7 per cent.)
Oxygen	= 31.1 per cent.	(theoretical value 30.7 per cent.)
Nitrogen	= 13.5 per cent.	(theoretical value 13.5 per cent.)

The infra-red spectrum of this material is shown in Fig. 2.

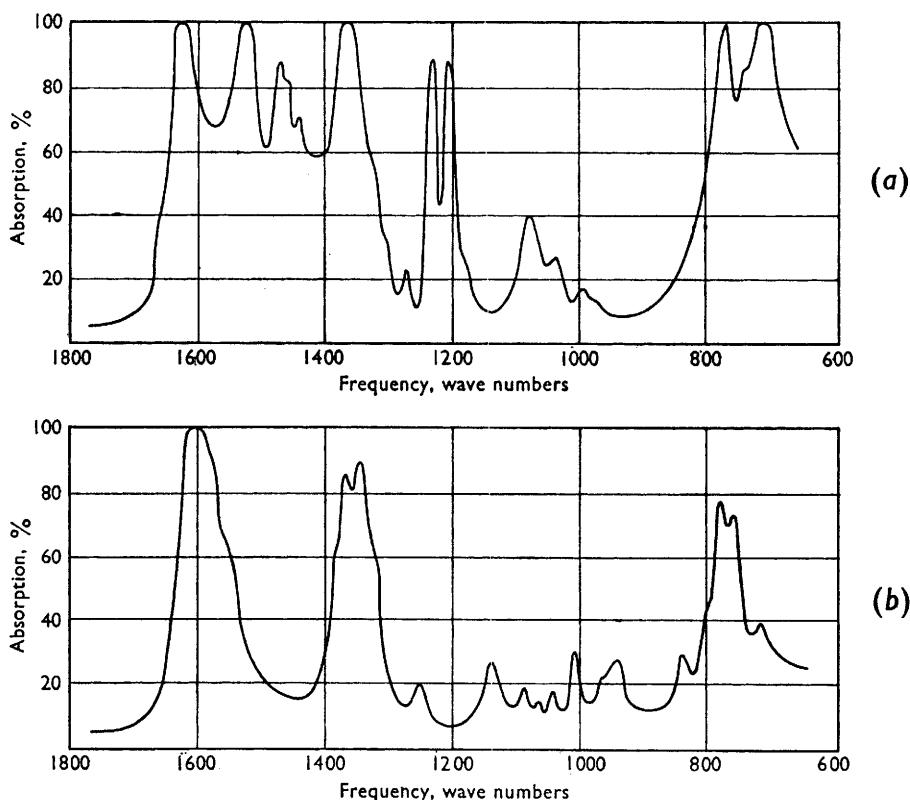


Fig. 2. Infra-red spectra of: (a) the diformyl derivative of hexamethylenediamine; (b) hexamethylenediamine dihydroformate. The spectra were prepared by the potassium bromide disc method; 1 per cent. of substance in potassium bromide; thickness of disc 1 mm

Mixtures of hexamethylenediamine dihydrochloride with (a) 5 per cent. by weight of the diformyl derivative, and (b) 5 per cent. by weight of the dihydroformate were now prepared, and their infra-red spectra were recorded. These spectra are shown in Fig. 3. Examination of these spectra did not point to the definite presence of either the diformyl or dihydroformate derivative of the hexamethylenediamine in the substance recovered from the chromatographic column.

Direct determination of the oxygen content by the Unterzaucher method, however, on the hexamethylenediamine dihydrochloride before and after passage through the chromatographic column yielded strong evidence that the material recovered from the eluate included an oxygen-containing constituent, as shown by the results in Table IV.

TABLE IV

OXYGEN DETERMINATIONS ON HEXAMETHYLENEDIAMINE DIHYDROCHLORIDE BEFORE AND AFTER PASSING THROUGH A CHROMATOGRAPHIC COLUMN

	Weight taken, mg	Titre of 0.2 N sodium thiosulphate, ml	Oxygen content, %
Hexamethylenediamine dihydrochloride	51.95	0.63	0.16
	51.18	0.89	0.23
Hexamethylenediamine dihydrochloride recovered from chromatographic column	51.88	4.31	1.11
	52.55	4.67	1.19
Blank on apparatus	—	0.24	0.06*
	—	0.21	0.05*

* These results are calculated on a weight of 52.0 mg.

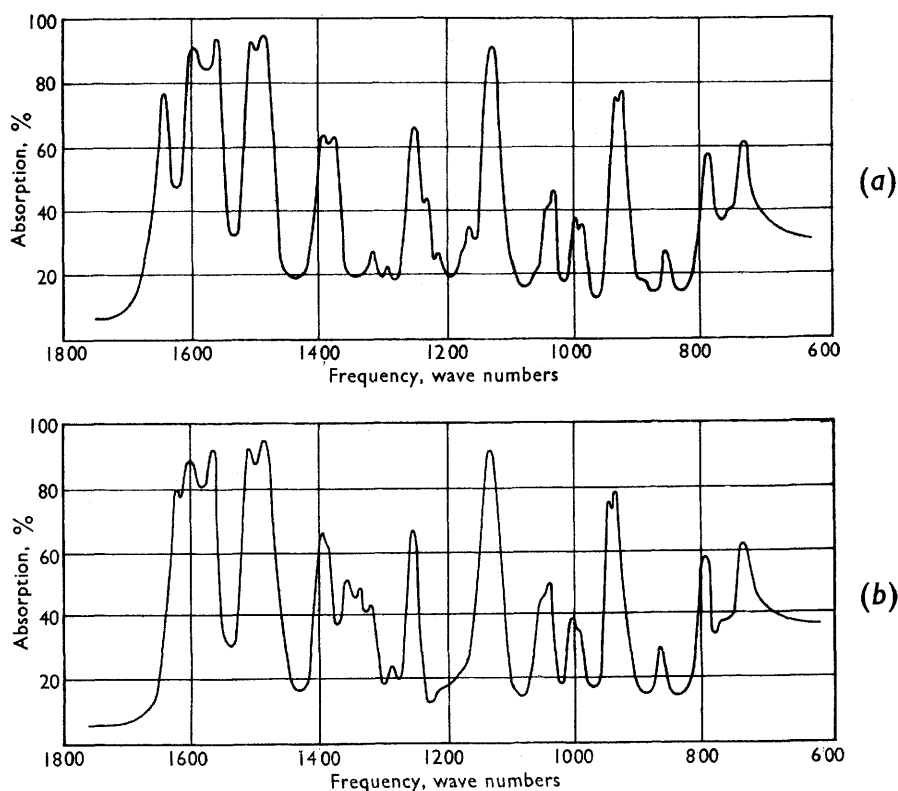


Fig. 3. Infra-red spectra of: (a) hexamethylenediamine dihydrochloride containing 5 per cent. of diformyl derivative; (b) hexamethylenediamine dihydrochloride containing 5 per cent. of dihydroformate. The spectra were prepared by the potassium bromide disc method; 1 per cent. of substance in potassium bromide; thickness of disc 1 mm

Evidence that the two substances were quite different was also provided by the application of the paper-chromatographic test described previously.¹

Fig. 4 shows the paper chromatograms of the hexamethylenediamine dihydrochloride before and after passing through the chromatographic columns, as seen under ultra-violet light. Whereas hexamethylenediamine dihydrochloride shows one definite spot, there is evidence of a further two spots in the hexamethylenediamine dihydrochloride that has been eluted from the column.

Although we have been unable to identify the contaminant produced as a result of the chromatographic test on hexamethylenediamine dihydrochloride, we believe that the following method would give a satisfactory resolution of mixtures of the three hydrochlorides of ϵ -aminocaproic acid, p -diaminodicyclohexylmethane and hexamethylenediamine.

The method is based on the assumption that the three hydrochlorides calculated as shown in the test are in the same proportions as in the mixture of hydrochlorides submitted to the test.

METHOD

REAGENTS—

sec.-Butanol, redistilled.

Formic acid, doubly distilled—The concentration of the doubly distilled acid is determined in the following manner. Approximately 2 ml of the acid are weighed into a stoppered weighing bottle, and the bottle is transferred to a 250-ml flask containing 100 ml of distilled water. The stopper is removed from the bottle under water and the solution is titrated with N sodium hydroxide solution to the end-point with phenolphthalein.

1 ml of N sodium hydroxide \equiv 0.04603 g of formic acid.

Ethanol, absolute.

Silver nitrate solution, 0.05 N.

Sodium hydroxide solution, 0.05 N.

sec.-Butanol - formic acid - water solvent—Seventy-five parts by volume of the redistilled *sec.-butanol* are mixed with 15 parts by volume of 90 per cent. w/w formic acid and 10 parts by volume of water. If the concentration of the doubly distilled formic acid differs from 90 per cent. w/w, then an adjustment must be made in the proportion of formic acid and water used in the preparation of the solvent. When the solvent has been prepared, it is finally checked in the following way. Five millilitres of the solvent are measured by means of a pipette into a conical flask containing 50 ml of water. The solution is titrated with N sodium hydroxide solution, with phenolphthalein as indicator. The titre should be 17.2 ± 0.1 ml, which represents a formic acid content of 15.8 ± 0.1 per cent. w/v.

Ethanol - water solvent—This solvent is prepared by mixing 75 parts by volume of distilled water and 25 parts by volume of absolute ethanol.

PROCEDURE FOR PREPARING CHROMATOGRAPHIC COLUMNS—

The columns used are of glass, approximately 12 to 13 mm in internal diameter, fitted with a sintered-glass disc just above the stop-cock. The length from the sintered-glass disc to the B14 ground-glass joint is 440 to 450 mm.

Before the columns are filled, the insides are coated with dimethyldichlorosilane, which is then decomposed with water in the usual way. The columns are then washed with acetone and dried in a current of air.

A slurry of cellulose powder (Whatman standard grade, ashless powder for chromatography) is prepared in the *sec.-butanol - formic acid - water solvent*. This slurry is poured into the column, which is gently tapped while doing so in order to ensure that no air bubbles are trapped in the slurry. The column stop-cock is then opened and the solvent is allowed to drain out slowly. Small amounts of the slurry are added continuously until a loosely packed column of 390 mm is obtained. During these operations a head of solvent is always maintained on top of the cellulose filling. Air must not be allowed to pass into the filling. The column is now compressed as tightly as possible with a flat-ended glass rod; this gives a tightly packed column 300 to 310 mm in length. The column, which must not be less than 300 mm in length, is now ready for use.

PROCEDURE FOR CHROMATOGRAPHIC SEPARATION—

A 0.2-g portion of the mixed hydrochlorides is weighed into a 10-ml beaker; 0.2 ml of distilled water and 0.3 ml of the doubly distilled formic acid are added, and the beaker is

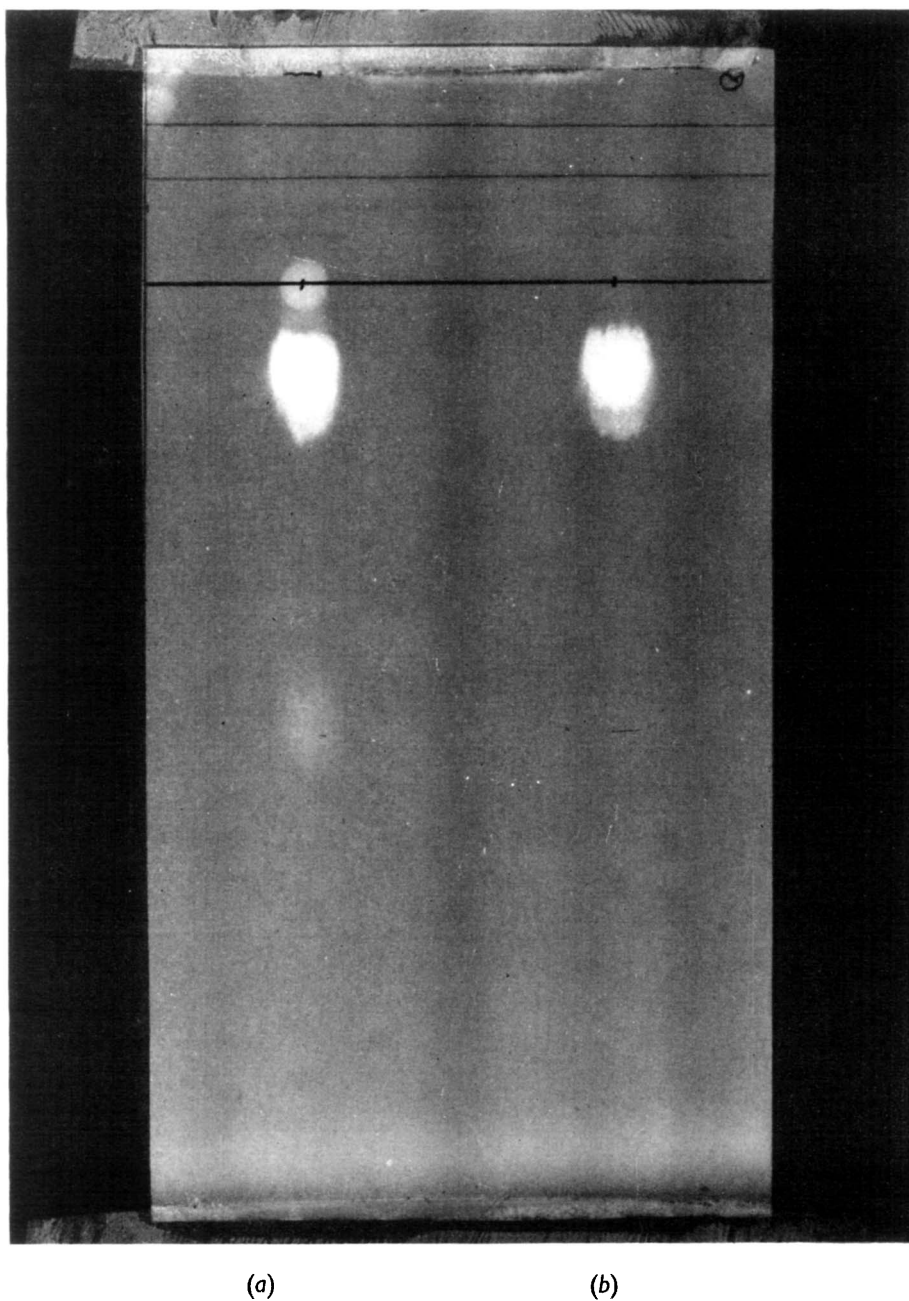


Fig. 4. Paper chromatograms, as seen under ultra-violet light, of hexamethylenediamine dihydrochloride (a) after passing and (b) before passing through a chromatographic column filled with cellulose

swirled occasionally until solution is attained. When the hydrochlorides have dissolved, 1.5 ml of *sec.*-butanol are added. The solution is now transferred to the top of the column by pouring through a small funnel with a drawn out stem. The beaker is washed three times with 1-ml portions of the *sec.*-butanol - formic acid - water solvent and finally the funnel is washed round with 1 ml of the solvent.

One hundred millilitres of the *sec.*-butanol - formic acid - water solution are placed in the solvent reservoir, which consists of a 500-ml round-bottomed flask with the neck drawn out to form a stem of $\frac{1}{4}$ inch in diameter. When the solvent washings have drained from the top of the column, the reservoir is placed on the top of the column so that the bottom of the stem is about 100 mm above the top of the cellulose packing. The solvent is allowed to flow slowly through the column and the eluate is collected in a 250-ml beaker.

When the *sec.*-butanol - formic acid - water solvent has just drained from the top of the column, the empty reservoir is replaced with one containing 100 ml of the ethanol - water solvent. The 250-ml beaker is replaced by a second clean one, and the solvent is allowed to drain through the column.

The first fraction, *i.e.*, the *sec.*-butanol - formic acid - water solution, contains ϵ -aminocaproic acid hydrochloride and *p*-diaminodicyclohexylmethane dihydrochloride, and the second fraction, *i.e.*, the ethanol - water solution, contains hexamethylenediamine dihydrochloride.

PROCEDURE FOR DETERMINING BASE HYDROCHLORIDES IN FRACTIONS—

After 20 ml of distilled water have been added to each 250-ml beaker, the solvent is removed by placing the beaker on a water bath. The residues are then dissolved in a small amount of water and re-evaporated. Evaporation with small amounts of water is repeated three or four times. Fifteen millilitres of water are then added and, after the beaker has been warmed on the water bath to ensure that complete solution has been obtained, the solution is allowed to cool.

The first fraction (*sec.*-butanol - formic acid - water fraction) is titrated with 0.05 *N* sodium hydroxide solution, with phenolphthalein as indicator. Then 1.5 ml of 2 *N* nitric acid are added, and the chloride ion is titrated electrometrically with 0.05 *N* silver nitrate solution. From the 0.05 *N* sodium hydroxide titre obtained, the weight of ϵ -aminocaproic acid hydrochloride is calculated, and from the difference between the 0.05 *N* silver nitrate titre and the 0.05 *N* sodium hydroxide titre, the *p*-diaminodicyclohexylmethane dihydrochloride is calculated.

To the second fraction are added 1.5 ml of 2 *N* nitric acid solution, and the chloride ion is titrated electrometrically with 0.05 *N* silver nitrate solution. From the titre obtained, the hexamethylenediamine dihydrochloride content of the mixed sample is calculated.

A blank determination is carried out.

CALCULATION OF RESULTS

The weight of each hydrochloride obtained in the test is divided by the total weight of hydrochlorides obtained and is then multiplied by 100 to give the percentage of hydrochloride in the original mixture, for example—

Weight of sample taken	0.20 g
Weight of ϵ -aminocaproic acid hydrochloride found	0.09 g
Weight of <i>p</i> -diaminodicyclohexylmethane dihydrochloride found	0.06 g
Weight of hexamethylenediamine dihydrochloride found	0.03 g
\therefore Total weight of hydrochlorides found = 0.09 + 0.06 + 0.03 =	0.18 g
\therefore ϵ -Aminocaproic acid hydrochloride in sample = $\frac{0.09}{0.18} \times 100$ =	50.0 per cent.
<i>p</i> -Diaminodicyclohexylmethane dihydrochloride in sample	
= $\frac{0.06}{0.18} \times 100$	33.3 per cent.
ϵ -Aminocaproic acid dihydrochloride in sample = $\frac{0.03}{0.18} \times 100$ =	16.7 per cent.

RESULTS

Application of the method described to various mixtures of the three hydrochlorides gave the results shown in Table V.

TABLE V

ANALYSIS OF KNOWN MIXTURES OF THE BASE HYDROCHLORIDE

Composition of mixtures					
ϵ -Aminocaproic acid hydrochloride		<i>p</i> -Diaminodicyclohexylmethane dihydrochloride		Hexamethylenediamine dihydrochloride	
Added, %	Found, %	Added, %	Found, %	Added, %	Found, %
30	29	—	—	70	71
89	89	—	—	11	11
50	50	25	25	25	25
10	8	15	16	75	76
—*	1	50	50	50	49
74*	73	12	13	14	14

* The composition of these mixtures was unknown to the operator at the time of the test.

We are indebted to Mr. H. A. Willis for the infra-red spectra shown in this paper.

REFERENCE

1. Clasper, M., Haslam, J., and Mooney, E. F., *Analyst*, 1955, **80**, 812.

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