Identification and analysis of plastics

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IDENTIFICATION AND ANALYSIS OF PLASTICS

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PREFACE

In writing a book on the analysis of plastics it is probable that the authors have worked on rather unconventional lines. We have not sought to bring together the work of a number of other authors in an attempt, and probably a fruitless attempt, to provide an unequivocal means of identifying all the plastics and plastics materials with which the investigator may be confronted.

On the contrary, we have tackled the problem from the point of view of two investigators, one a spectroscopist and the other an analytical chemist, who over a period of eighteen years, have worked together in very close collaboration, seeking to weld together both chemical and physical methods of examination of polymers etc.

Moreover, it must be realised that we are enthusiasts for this combined method of approach, often very rewarding, when the individual approach, for example, by chemical procedures alone might be quite unrewarding.

Further, it is the case that the bias in this book is towards the examination of the products and problems of the company with which we have been concerned.

We trust, however, that the practical methods we have worked out to solve our own problems will help other investigators in rather different fields of plastics analysis in solving theirs.

It should be realised that the emphasis throughout the book is on principle and we have tried to incorporate as many new principles as possible.

Each chapter is prefaced by an introduction linking the essential features of the chemical and infra-red methods of examination described in the chapter itself. These methods of test are described whenever practicable, by full working details.

We should like to acknowledge our indebtedness to the Directors of Imperial Chemical Industries Ltd., (Plastics Division) for permission to publish this work and to make use of the information gained as a result of our service with the company. Further, we wish to thank all those members of the Plastics Division, and they are very many, although principally in the Infra-red and Analytical sections of the firm, who have helped and inspired us over the years.

The problems they have submitted and assisted in solving have contributed in no small measure to this effort on our part.

In addition, we are grateful to the authors of other standard text books in this field, notably the following: D. Hummel, *Kunstoff-, Lack- und Gummi-Analyse*, Carl Hanser Verlag, Munchen, 1958; G. M. Kline, *Analytical Chemistry of Polymers*, Interscience Publishers, New York and London, Part 1, 1959: Part 2, 1962: Part 3, 1962; K. Thinius, *Analytische Chemie der Plaste*, Springer Verlag, 1952; W. C. Wake, *The Analysis of Rubbers and Rubber-like Polymers*, Maclaren and Sons, London 1958.

Welwyn Garden City, 1965

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QUALITATIVE ANALYSIS

CHEMICAL QUALITATIVE ANALYSIS

The first part of this chapter is concerned with the chemical detection and semi-quantitative determination of elements such as nitrogen, sulphur, phosphorus, chlorine and fluorine in plastic materials. Solubility tests and procedures involving burning and heating are dealt with, and finally specific chemical tests for certain polymers etc., e.g. melamine, polyethylene terephthalate, polyvinyl chloride, formaldehyde and so on are described.

The second part of this chapter deals with the interpretation of the infra-red spectrum of an unknown substance; this interpretation is rendered much more satisfactory if the nature and rough concentration of the elements present are already known.

For substances containing only carbon and hydrogen, it is shown how the presence of chemical groups such as methyl groups and benzene nuclei may be established; the presence of these structures may also be ascertained in more complex substances containing additional elements, but in these compounds attention is directed particularly to the way in which the mode of combination of the additional elements may in many cases be deduced from examination of the spectrum.

With this knowledge of the chemical groups present in a compound, the chemist may make deductions as to the nature of the unknown substance. This procedure is recommended to that of matching unknown spectra against standards without regard to the chemical information available from the spectrum.

In the first place it is important to realise the particular point of view from which this chapter is written.

Essentially we are concerned with the preliminary qualitative examination of polymers, polymer preparations, plasticisers and the like, which may be submitted for test and which may have their origin in all parts of the globe. The samples may be submitted in innumerable forms, i.e. as polymer powders, as sheet, as rod, tube or film and as finished articles. Moreover, specific questions may be asked about the samples, i.e.

questions that do not always involve the complete identification of all the constituents of e.g. a polymer preparation. That complete identification might be very prolonged and involve the isolation and identification of a polymer, or copolymer, or blend of polymers, the isolation of a mixed plasticiser and the resolution of this mixed plasticiser into its individual components, the isolation and identification of a stabiliser, filler, anti-oxidant or surface active agent and so on.

Moreover, a great deal of the preliminary work in the identification of plastic materials is merely concerned with separation procedures, that serve to isolate components for subsequent infra-red or other final identification.

In some respects, one of the most useful papers on the subject of identification of synthetic resins and plastics is that of T. Gladstone Shaw.[1] Shaw seeks to develop systematic procedures for the separation of resins from solvents, plasticisers etc., for the separation of mixtures of resins into individual resins, for the classification of individual resins into groups, and for the identification of resins within a group.

In our experience, however, strict application of this procedure would fail to answer a lot of questions submitted to the analytical chemist in the plastics industry, e.g. is a nylon type polymer nylon 6 : 6 or nylon 6 : 10 or a copolymer or terpolymer? Is a given chlorine containing polymer polyvinyl chloride or is it a copolymer of vinyl chloride with a very small proportion of vinyl acetate?

It is for reasons such as this that we regard our initial qualitative work as being preliminary work that can provide helpful information about a polymer or polymer preparation. Often enough it will provide useful clues as to the subsequent quantitative tests that may have to be carried out, and in many cases, if supplemented by infra-red evidence on the right preparations, will enable a whole host of questions to be answered with great speed.

Our purpose, therefore, is to describe those tests that, in our experience, have proved to be most useful, in providing the qualititative information we have in mind.

By far the most important test is that for 'additional elements' in a plastic material, i.e. elements other than carbon, hydrogen and oxygen such as sulphur, fluorine, phosphorus, chlorine and nitrogen, whether or not our examination is carried out directly on a polymer composition, or on a separated polymer, or plasticiser, or other constituent of a polymer composition.

For many years this test for additional elements was carried out by means of the sodium fusion test.

Experience has shown however, that this test as ordinarily carried out, is often quite inadequate. One good reason is that the analytical chemist in the plastics industry is not, as a rule, concerned solely with the differentiation of simple polymers such as polyvinyl chloride, polyethylene terephthalate, polytetrafluoroethylene, polymethyl methacrylate and the like. He may, for instance, meet a preparation that, by the sodium fusion test, may obviously contain a high proportion of chlorine and yield no

evidence of nitrogen. The behaviour would be quite consistent with that of a blend of a high proportion of polyvinyl chloride and a proportion, small but not insignificant, of a terpolymer of butadiene, styrene and acrylonitrile. The overall percentage of nitrogen might only be of the order of 0·3% but even this small amount should be detected, because calculated to acrylonitrile it will represent a significant amount of this constituent in the composition though missed by the sodium fusion test.

Then again, in the qualitative examination of certain polymers it may be quite important not to miss quite small proportions of sulphur; the detection of this element may give a clue to the presence of a surface active agent or other additive.

Moreover, by its very nature, the sodium fusion test cannot be a very efficient or quantitative process.

In our laboratories it was thought desirable to approach the whole problem of detection of additional elements in a plastic material from quite a new angle, and to provide tests that, at the same time, would furnish, broadly speaking, semi-quantitative information. The method is known as the Oxygen Flask Combustion Method.[2,3] In this method, the plastic material, wrapped in filter paper, is ignited electrically and burnt in a closed glass flask filled with oxygen in the presence of sodium hydroxide solution as absorbent. Appropriate tests for the additional elements are then made on the sodium hydroxide solution.

A full description of the method is given below.

OXYGEN FLASK COMBUSTION METHOD

Apparatus

The complete combustion flask and firing adapter together with the firing spark source are shown in Fig. 1.1 and a more detailed diagram of the firing adapter together with the necessary constructional details are shown in Fig. 1.2.

The H.F. tester (model T.1) for producing the spark used to initiate the combustion is manufactured by Edwards High Vacuum Company Limited, Crawley, Sussex. It is mains operated and relatively inexpensive.

The leads from the H.F. tester to the firing terminals may be of any convenient length, allowing remote control firing from behind a suitable safety screen. The position of the platinum gauze combustion basket in relation to the ancillary firing electrode is as shown in Fig. 1.2, so that the flame from the burning sample does not play on the platinum wire, which, by a cooling effect, may on occasion lead to the formation of unburnt carbon in the flask. It is important that the joint between the firing adapter and the combustion flask should show no signs of leakage.

General reagents

Filterpaper. Whatman No. 541 filter paper. When not in use, this filter

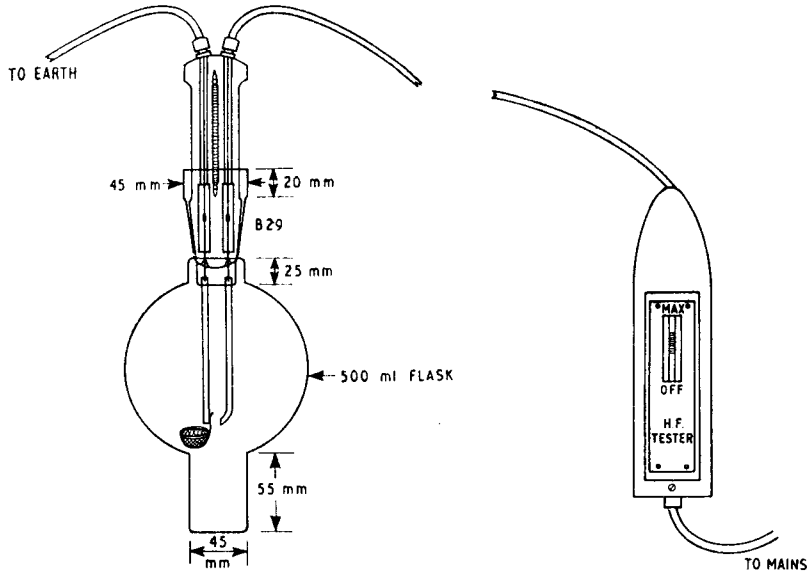

Fig. 1.1. Combustion unit and spark source. (Flask and adapter made of Pyrex glass)

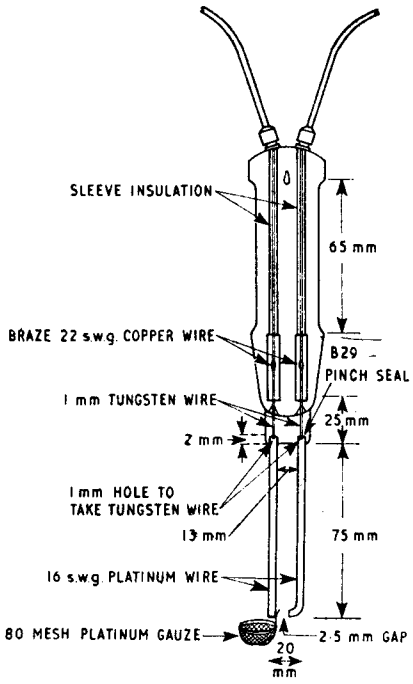

Fig. 1.2. Firing adapter

paper is stored in a sealed container out of contact with the laboratory atmosphere.
Cotton wool B.P.C. Super Quality.
Sodium hydroxide N.

Procedure

Weigh out approximately 20 mg of sample and transfer it to the centre of a small piece of the Whatman No. 541 filter paper weighing approximately 0·1 g. Fold the filter paper so that the sample is completely enclosed, and, before making the final fold, insert a small wick of cotton wool weighing about 6 mg.

Prepare the combustion vessel by washing the flask and adapter and heating the end of the platinum wire and the basket to red heat in a bunsen flame. Place 5 ml of N sodium hydroxide solution in the bottom of the flask to act as absorbent. Fill the flask with oxygen and insert the stopper. Place the wrapped sample in the platinum basket and twist the cotton wool wick so that it lies between the basket and the ancillary firing electrode. Remove the stopper from the flask and replace it with the adapter containing the sample. Seal the joint with a suitable amount of distilled water, and attach the retaining springs. Attach the electrical and earth leads to the adapter and place the safety screen in front of the combustion vessel, or, alternatively, arrange the whole apparatus inside a suitable safety box.

Switch on the H.F. tester to ignite the cotton wool and sample and allow to burn to completion.

Set the flask aside for 15 min, shaking occasionally to ensure good absorption of the combustion products, then open up the flask and add 20 ml of distilled water and mix the contents thoroughly.

The test solution, prepared as above, has a volume of approximately 25 ml. Aliquots of this solution are taken for the detection of the individual elements by the colorimetric and turbidimetric methods detailed below. For comparison purposes in the tests, prepare a blank test solution by carrying out the combustion procedure on the filter paper and cotton wool only.*

CHLORINE

Reagents

Ammonium ferric sulphate solution.
Dissolve 12 g of Analar ammonium ferric sulphate in water and add 40 ml of Analar nitric acid. Dilute to 100 ml and filter.
Mercuric thiocyanate solution.

* The data given in the test procedure are for a flask of the type shown in Fig. 1.1. It may, on occasion, be more convenient to use a lipped conical combustion flask, provided that appropriate calibration is made.

A further point concerns the combustion process. If the platinum gauze has fused and developed a hole during previous combustions, this hole should be covered up with a fresh piece of gauze for the next test. When the gauze can no longer be used it is returned to the makers for recovery. The cost of an individual test is negligible.

Dissolve 0·4 g of mercuric thiocyanate that has been recrystallised from ethanol in 100 ml of absolute ethanol.

Procedure

Transfer 5 ml of the test solution to a 50 ml beaker and add 1 ml of ammonium ferric sulphate solution. Mix the solution and add 1·5 ml of mercuric thiocyanate solution. When chlorine is present in the sample an orange red colour will be developed in the test solution. If a semi-quantitative estimation of chlorine is required, set the solution aside for 10 min, and measure the optical density of the test solution against the blank solution at 460 mμ in 2 cm cells.

Useful calibration figures for the examination of plastic materials are given below.

Chlorine in Plastic Material. %	Optical Density $D^{2\,cm}_{460\,m\mu}$ measured against blank
1	0·4
2	0·75

SULPHUR

Reagents

Hydrochloric acid N.

Precipitating reagent solution A.

Dissolve 0·2 g of peptone in 50 ml of 1 % barium chloride ($BaCl_2 2H_2O$) solution. Buffer to a pH of 5·0 with 0·02 N hydrochloric acid, add 10 g of sodium chloride (Analar) and dilute to 100 ml. Heat on a water bath for 10 min and add a few drops of chloroform. Filter if necessary.

Precipitating reagent solution B.

Dissolve 0·4 g of gum ghatti in 200 ml of distilled water by warming slightly. When solution is complete, add 2·0 g of barium chloride ($BaCl_2 2H_2O$). Filter if necessary.

Store solutions A and B separately, and prepare the final reagent just before use by diluting 10 ml of solution A to 100 ml with solution B.

Hydrogen peroxide. 100 volume. Analar.

Procedure

Transfer 5 ml of the test solution to a 6 × 1 in test tube, and add 2 drops of 100 volume hydrogen peroxide and then 1·2 ml of N hydrochloric acid. Mix well and add 2·0 ml of precipitating reagent with continued shaking. A distinct turbidity will be produced in the mixed solution if sulphur is present in the sample; the blank test under the same

conditions will be perfectly clear. If a semi-quantitative estimation of the sulphur content is required, add 5 ml of distilled water to both blank and test solutions, mix and set aside for 30 min. Mix the solutions and measure the optical density of the test solution in a 4 cm cell at 700 mμ with the blank solution in the comparison cell.

Useful calibration data for the examination of plastic materials are given below.

Sulphur in Plastic Material. %	Optical Density $D^{4\text{ cm}}_{700\text{ m}\mu}$ measured against blank
1	0·2
2	0·4

NITROGEN

Reagents

Resorcinol. Analar.
Acetic acid glacial.
Ammonium ferrous sulphate. Analar.

Procedure

Weigh 0·1 g of resorcinol into a clean dry 50 ml beaker and dissolve in 0·5 ml of glacial acetic acid, add 5 ml of the test solution, and after mixing, add 0·1 g of ammonium ferrous sulphate. Carry out the same test on the blank test solution. The development of a green colour in the sample test solution, compared with a pale yellow in the blank, indicates the presence of nitrogen in the sample.

If a semi-quantitative estimation of the nitrogen content of the sample is required, set both sample and blank solutions aside for 20 min. Add 10 ml of distilled water to each, mix and measure the optical density of the sample solution against the blank at 690 mμ in a 4 cm cell. In our experience, the blank in this test is low, giving an optical density of 0·07 measured against water.

Useful calibration data for the examination of plastic materials are given below.

Nitrogen in Plastic Material %	Optical Density $D^{4\text{ cm}}_{690\text{ m}\mu}$ measured against blank
1	0·6
2	1·0

PHOSPHORUS

Reagents

Ammonium molybdate solution.
Dissolve 10 g of Analar ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in about 70 ml of water, and dilute to 100 ml. Add this solution with stirring to a cooled mixture of 150 ml of sulphuric acid and 150 ml of water.
Ascorbic acid. B.D.H. laboratory reagent grade.

Procedure

Transfer 2 ml of the test solution to a 100 ml beaker. Add 40 ml of distilled water and 4 ml of ammonium molybdate solution. Mix thoroughly, then add 0·1 g of ascorbic acid, and boil the solution for 1 min. Cool in running water for 10 min and dilute to 50 ml with distilled water. Treat the blank solution in a similar manner. When phosphorus is present in the sample, a blue colour will be developed in the test solution as compared with a pale yellow in the blank. If a semi-quantitative estimation of the phosphorus is required, measure the optical density of the test solution against the blank solution at 820 mμ in 2 cm cells.

Useful calibration data for the examination of plastic materials are given below.

Phosphorus in Plastic Material. %	Optical Density $D^{2\,cm}_{820\,m\mu}$ measured against blank
1	0·45
2	0·95

FLUORINE

Reagents

Buffered alizarin complexan solution.
Weigh 40·1 mg of 3-aminomethylalizarin-NN-diacetic acid (Hopkins and Williams Ltd.) into a beaker and add 1 drop of N sodium hydroxide and approximately 20 ml of distilled water. Warm the solution to dissolve the reagent, cool and dilute to 208 ml. Weigh into another beaker 4·4 g of sodium acetate ($CH_3 \cdot COONa \cdot 2H_2O$) and dissolve in water. Add 4·2 ml of glacial acetic acid and dilute to 42 ml. Pour this sodium acetate solution into the alizarin complexan solution and mix to give the final buffered alizarin complexan solution.
Cerous nitrate 0·0005 M.
Dissolve 54·3 mg of cerous nitrate [$Ce(NO_3)_3 \cdot 6H_2O$] in water and dilute to 250 ml.

Procedure

Transfer 20 ml of distilled water and 2·4 ml of buffered alizarin complexan solution to a 50 ml beaker. Add 1 ml of test solution and mix by swirling the solution. Finally add 2 ml of cerous nitrate solution and mix again. Treat the blank solution in a similar manner. When fluorine is present in the sample a mauve colour will be developed in the test solution compared with the pink coloured blank solution. If a semi-quantitative estimation of fluorine is required, set the solution aside for 10 min and measure the optical density of the test solution against the blank solution at 600 mμ in 1 cm cells.

Useful calibration data for the examination of plastic materials are given below.

Fluorine in Plastic Material. %	Optical Density $D^{1\,cm}_{600\,m\mu}$ measured against blank
1	0·07
2	0·135

Although bromine and iodine are not normally found in plastic materials, the original paper includes information about the fluorescein test given by both iodides and bromides and the starch test for iodine. Moreover, it should be realised that iodides and bromides, if present in the oxygen flask combustion products, will give positive results in the mercury thiocyanate test for chloride.

For most purposes, application of the procedure as described provides sufficient information about the sample under test, but, if required, the sensitivity of any of the individual tests may be significantly increased.

This may be accomplished by repeating the combustion, absorbing the products in 5 ml of 0·2 N sodium hydroxide and making a direct test for the particular element on this solution without dilution and with appropriate calibration.

Moreover, it should be realised that a lot of time may be saved in the actual tests by using the solid reagents in the form of solid pellets, of known weight, as sold by Messrs. Ridsdale & Co. Ltd., Newham Hall, Middlesbrough, and dispensing the liquid reagents from dispensers e.g. Miscomatic dispensers as manufactured by Microchemical Specialties Co., Berkeley 10, California.

SOLUBILITY

The analytical chemist in the plastics industry can often provide useful information about a test preparation by obtaining knowledge of its behaviour towards solvents, or solutions that attack the substance, e.g. polytetrafluoroethylene may be characterised by its inertness towards almost all chemical solvents.

Very useful information about the solubility or otherwise of a whole

host of polymers etc. in various solvents is provided in text books such as those of Collins[4] and Marsden[5]. In practice, however, it is probably much more realistic to provide information about those solvents or solutions that, over the years, have proved to be useful in actual determinations on polymers or polymer preparations. They can all be adapted by the competent analyst to preliminary qualitative examination of miscellaneous preparations, provided he takes care to work at room temperature, and at temperatures up to boiling temperature of the solvent or attacking solution.

This information is summarised in Table 1.1.

Table 1.1

Polymer or Polymer Preparation	*Solvent or solution used*	*Purpose*
Polyvinyl chloride	Ethylene dichloride	Determination of solution viscosities and K values
Polyvinyl chloride composition	Tetrahydrofuran	Recovery of polymer or copolymer free from impurities
Polyvinyl chloride compositions	Ethylene dichloride	Determination of lead stabilisers
Vinyl chloride copolymer	Methyl ethyl ketone	Determination of acidity
Vinyl chloride/vinylidene chloride copolymer compositions	Tetrahydrofuran	Recovery of polymer or copolymer free from impurities
Vinyl chloride/vinyl acetate/maleic acid terpolymer	Pyridine	Determination of acid groups
Vinyl chloride/methacrylic acid copolymer	Pyridine	Determination of acid groups
Vinyl chloride/acrylamide copolymer	Acetic anhydride	Titration of acrylamide
Polyvinyl chloride/chlorinated polythene blends	Carbon tetrachloride or chloroform	Solution and separation of chlorinated polythene
Polymethyl methacrylate	Acetone	Plasticiser determination
	Acetone	Chemical determination of U.V. absorber
	Chloroform	U.V. determination of U.V. absorber
	Chloroform	Residual monomer determination
	Acetone	Mercaptan determination
	Chloroform	Relative viscosity determination

Table 1.1—*continued*

Polymer or Polymer Preparation	*Solvent or solution used*	*Purpose*
	Acetone	Butyl lactate determination also dibutyl citric acid determination
	Chloroform or isopropyl alcohol	Determination of residual benzoyl peroxide
Polymethyl methacrylate (emulsion polymerised)	Acetone	Stearic acid determination
Polymethyl methacrylate moulding powder containing lead pyrophosphate	Ethylene dichloride	Determination of lead pyrophosphate
Polymethyl methacrylate and related polymer preparations	Phenol and Hydriodic acid	Determination of alkoxyl groups
Methyl methacrylate/ethyl acrylate copolymer containing opacifying agent (?)	Acetone	Isolation of butadiene styrene copolymer used as opacifying agent (?)
Methyl methacrylate/ methacrylic acid copolymer	Acetone Isopropyl alcohol	Potentiometric titration of acid groups
Methyl methacrylate/styrene copolymer	Methylene dichloride	Residual benzoyl peroxide determination
Polymethyl α-chloroacrylate	Methylene dichloride	Determination of polymer
Polyethylene terephthalate	*o*-chlorophenol Mixtures of phenol and cresols	Determination of relative viscosity
	o-cresol and chloroform	Determination of end groups
	Phenol and tetrachloroethane	U.V. determination of U.V. absorbers
	Monoethanolamine	Breakdown to yield crystalline derivative for identification
Polycarbonates	Monoethanolamine	Breakdown to yield constituent phenol
Nylon and related polymers	90% Formic acid	Determination of relative viscosity
	90% Formic acid	Direct chromatography
	Hydrochloric acid (1 : 1) either in sealed tube or boiled under reflux	Chemical or chromatographic examination of breakdown products
	Phosphoric acid with distillation	Determination of acetyl end groups
Nylon (methoxy methyl modified)	Alcohol	Direct determination of free formaldehyde

Table 1.1—*continued*

Polymer or Polymer Preparation	*Solvent or solution used*	*Purpose*
Polythene	Tetrahydronaphthalene	Determination of relative viscosity
	Toluene	Determination of anti-oxidants, additives and contaminants e.g. oxidised polythene
	Methyl cyclohexane	Determination of anti-oxidants and additives
Polythene/polyisobutene blends	Toluene	Determination of polyisobutene
Polystyrene	Chloroform	U.V. Spectrophotometric examination
Polystyrene	Acetone	Determination of dibutyl citric acid
Styrene/acrylonitrile copolymer	Chloroform	U.V. Spectrophotometric examination
Acrylonitrile/styrene copolymer Acrylonitrile/butadiene copolymer blends	Acetone	Determination of acrylonitrile/styrene copolymer by taking advantage of its solubility
Phenol formaldehyde Phenol/cresol formaldehyde resins	Sodium hydroxide solution	Determination of free phenols
Phenol formaldehyde moulding powder	Acetone	Determination of resin
Phenol formaldehyde mouldings	2-Naphthol in sealed tube	Determination of filler
Urea formaldehyde and melamine formaldehyde resins	Acetic acid	Characterisation of urea and melamine after breakdown
Urea formaldehyde and melamine formaldehyde resins and compositions	0·1 N Hydrochloric acid	Determination of melamine by U.V. spectrophotometry
Urea formaldehyde compositions	1% v/v Hydrochloric acid	Detection of urea in breakdown products by urease
Urea formaldehyde resins	1 : 1 Phosphoric acid	Determination of formaldehyde
	Benzylamine	Determination of urea
Thiourea formaldehyde resins	Acetic acid	Detection of thiourea
Epoxy resins	Conc. sulphuric acid	Application of Foucry's tests for epoxy resins
Polyvinyl alcohol	Water	Cloud point determination