The Examination of Toys for Celluloid

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The testing of the plastic for nitrate, the extraction and identification of camphor and the use of manner and time in which the plastic burns as tests for celluloid are described.

The Toys (Safety) Regulations, 1967, S.I. No. 1157*, decreed that after the 31st October, 1967, a toy shall not, either wholly or in part, be made of or impregnated with cellulose nitrate.

When used in toys, cellulose nitrate is plasticised with camphor to form celluloid, the proportion of camphor varying from 24 to 30 per cent. Other plasticisers have been used in the manufacture of celluloid but they are unlikely to be met with in toys.

A rapid, simple method is described for the examination of plastics for the presence of celluloid when infra-red spectroscopy or pyrolytic gas chromatography are not available. The procedure involves the qualitative testing of the plastic for nitrate using diphenylamine/sulphuric acid reagent, the extraction and subsequent identification of the camphor by gas-liquid chromatography, and the examination of the manner and time in which the plastic burns.

Apparatus

1. Gas Chromatograph: Varian Aerograph, model 1522/1B.
2. Recorder: by Leeds and Northrup, with 1 mV full-scale deflection (Chart speed 15 inches/hour).
3. Flame ionisation detector.
4. Columns: *a.* 5 ft. × $\frac{1}{8}$ in. o.d., stainless steel column, packed with 10 per cent. Carbowax 6000 + 5 per cent. potassium hydroxide, on Celite (100 to 120 mesh).
   b. 5 ft. × $\frac{1}{8}$ in. o.d., stainless steel column packed with 5 per cent. silicone SE.30 on Chromosorb W. (50 to 60 mesh).

Reagents

1. *Diphenylamine:* AR grade.
2. *Sulphuric acid:* concentrated, AR grade.
3. *Stannous chloride Soln.:* 10 per cent. w/v.
4. *Chloroform:* AR grade (redistilled).

* Obtainable from H.M. Stationery Office, London.

Procedure

EXTRACTION AND IDENTIFICATION OF CAMPHOR

For the rapid detection of the presence of camphor, mix about 0·2 g of the plastic with chloroform, and evaporate the chloroform to low bulk, when the odour of camphor, if present, can be readily recognised.

For the GLC identification of camphor, place 0·2 g of finely-chopped plastic in a glass-stoppered, 10-ml standard flask and make to volume with chloroform. Shake the mixture and allow it to stand for two hours. Inject 4 microlitres on to the GLC (Carbowax) column under the conditions given below.

Flow Rates

Carrier gas (nitrogen)	30 ml per min.
Hydrogen	20 ml per min.
Air	300 ml per min.

Equipment Data

Column 170° C: Injector 250°C: Detector 210°C. Range 10; attenuation 32 (equivalent to $9{\cdot}6 \times 10^{-9}$ amps.).

NITRATE

Place a small piece (10 sq. mm) of the plastic in a test tube and wet it with one drop of distilled water. Add 3 ml of a solution of 25 mg of diphenylamine in 25 ml concentrated sulphuric acid. In the presence of nitrate, a blue colour rapidly develops, diffusing away from the plastic. Shake the tube and allow it to stand for five minutes. If the solution is blue, divide it into two parts. To one portion add 10 ml of distilled water. If the blue colour remains or a purple colour develops, carefully add to the second portion a few drops of stannous chloride solution. Mix and dilute the solution with 5 ml of water. After about 20 minutes a yellow or orange precipitate develops in the presence of nitrate.

CELLULOID

Cut a strip of the plastic, about 1 cm wide, to weigh one gramme. Hold the strip horizontally, ignite one end and record the time required to burn the strip. Observe the manner in which it burns and the nature of the residue.

For further evidence of the presence of celluloid, take 0·2 g of suspected celluloidal plastic and dissolve it in 5 ml of acetone by gentle warming. Pour the solution into 10 ml of distilled water in a porcelain dish, and dry the mixture on a water-bath. Transfer the residue to an extraction thimble and extract it for two hours with chloroform. Evaporate the solution to about 1 ml, and inject 4 microlitres on to a 5 per cent. silicone SE.30, GLC column under the conditions used for the Carbowax column (but using range = 1 and attenuation = 4).

Results and Discussion

Camphor: Of the solvents used, chloroform was found to achieve the most efficient extraction of the camphor. To avoid loss of camphor, heating should not be used in the extraction stage. Some typical peaks obtained for camphor on the Carbowax column are shown in Figure 1.

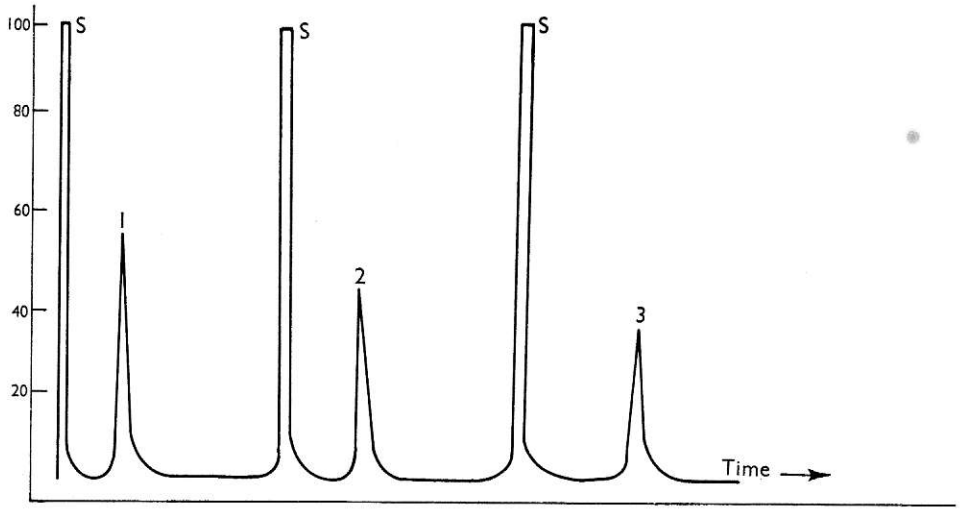

Fig. 1. Characteristic peaks obtained by GLC from solutions of celluloid.
S Solvent peak
1. Standard camphor peak
2. Ping-pong ball extract
3. Extract from doll suspected of containing celluloid

The retention time for camphor on this column is 1·33 minutes. The low sensitivity and high concentration of camphor are used to give a better separation of the camphor and solvent peaks. An approximate quantitative estimation of celluloid is possible but because the efficiency of the extraction cannot be determined at present, it is impossible to judge the accuracy of any figures obtained.

A variety of other plastics including polypropylene, polyethylene, perspex, fluon, P.V.C., bakelite and co-polymer of propylene and ethylene were extracted and examined under identical conditions. The results showed the absence of camphor and no interfering peaks.

Nitrate: The development of the blue colour is not specific for nitrate. The colour will develop in the presence of such oxidising agents as chromates, etc., which may be present in pigments used to colour the plastic. However, the use of stannous chloride solution followed by dilution will distinguish between the colour due to other oxidising agents and that due to the presence of nitrate.

The diphenylamine reagent should be freshly prepared before use since it readily develops a blue colour from atmospheric oxidation.

Celluloid: The rate of burning and the manner of burning, may, with experience, be used as a means of distinguishing celluloid from other plastics. Celluloid burns very vigorously (less than 20 seconds for 1 g) to give a very fine "thread-like" ash. The majority of the other plastics examined require much longer to burn (more than 90 seconds) and drip while burning, to leave a wax-like residue.

The type of peak patterns obtained when extracts of toys are examined by GLC with the silicone column are shown in Figure. 2.

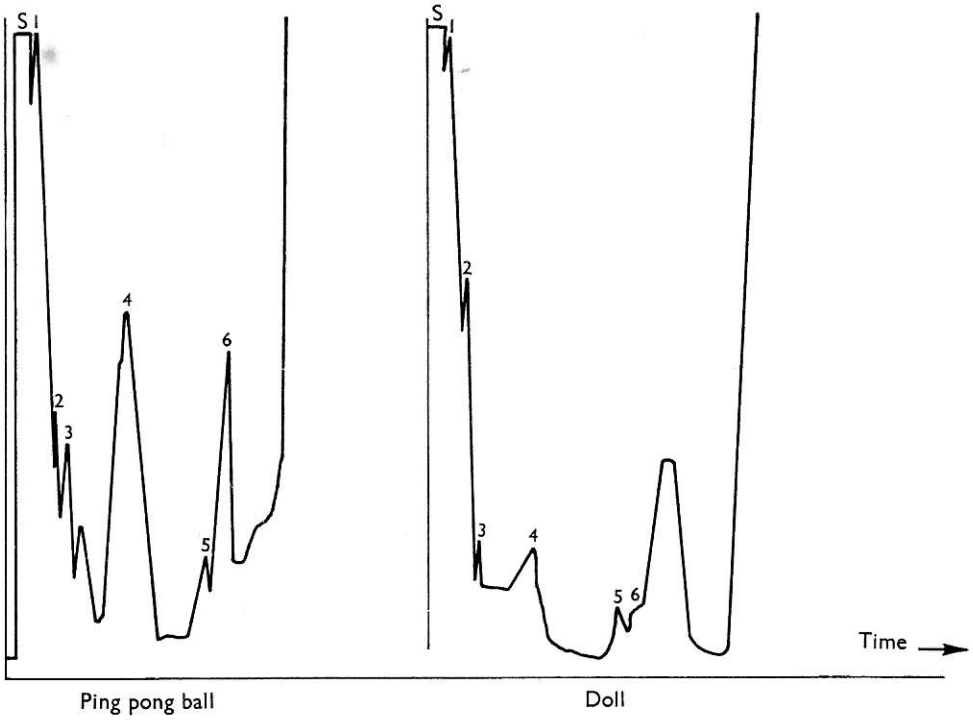

Fig. 2. Characteristic peaks obtained by GLC from toys suspected of containing celluloid.

Peaks 1 to 6 in Figure 2 were obtained from a ping-pong ball and a doll suspected of containing celluloid. In a similar examination of other plastics it was found that they did not dissolve in acetone and no corresponding peaks were observed.

The retention time of camphor on this column is less than 0·25 min. and hence it is difficult to separate it from the solvent peak.