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Investigation into the Sampling and
Analysis of Solder Fume Part V –
Development of a Sampling
Method for Resin Acids

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SUMMARY

An investigation was carried out to develop a personal sampling method for solder fume with the aim of obtaining both qualitative and quantitative information. Although both volatile and particulate fractions are present in solder fume, the sampling method was developed primarily to investigate the particulate matter which is made up largely of resin acids. The solder fume was sampled onto a membrane filter from which the resin acids were recovered by solvent extraction. The samples were then methylated and analysed by gas chromatography. Solder fume is usually generated as a fairly tight plume rising from the soldering iron tip, and so a field comparison was carried out between samplers located in the traditional position on the lapel and those located in the breathing zone to investigate whether the lapel samples were sampling representatively. In addition, because solder fume is now regarded as a respiratory sensitiser, some short-term, high flow-rate 10 minute sampling was carried out enabling a comparison of peak concentration levels with those obtained from a longer time-weighted average sampling period.

Specific achievements include.

1. Development of a sampling method for the determination of atmospheric solder fume levels by measurement of resin acids. The advantages of this method include the following.
 - Individual and total resin acid concentrations can be determined.
 - The compact sampling device allows placement in the breathing zone.
 - The method sensitivity is sufficient for both 8-hour and 10-minute sampling.
 - The method can be used in other factory atmospheres where resin acids may be present eg Hot Melt Glues.
 - The method can be easily adapted to sample volatile components.
2. Using the developed method to show that levels of solder fume increase markedly with soldering iron temperature, and hence solder fume levels can be minimised by reducing iron temperature to the minimum necessary for efficient soldering.
3. Using the developed method in field trials to show that solder fume levels in the breathing zone are up to 5 times higher than those on the lapel.

CONTENTS

1. INTRODUCTION AND OBJECTIVES	5
2. GAS CHROMATOGRAPHIC ANALYSIS OF VOLATILE FRACTION	6
2.1 Qualitative Analysis	6
2.2 Quantitative Analysis	7
3. GAS CHROMATOGRAPHIC ANALYSIS OF PARTICULATE FRACTION	9
3.1 Optimisation of Sample Preparation Method	9
3.1.1 Revised Methylation Procedure	10
3.1.2 Comparison of Methods	10
3.2 Optimisation of Chromatographic Conditions	11
3.3 Qualitative Analysis	12
3.4 Quantitative Analysis	12
3.4.1 Methyl Stearate Standards	13
3.4.2 Abietic Acid Standards	15
3.4.3 Dehydroabietic Acid Standards	16
3.4.4 Combination of Standards	16
3.4.5 Relative FID Response Factors	18
4. GENERATION OF SOLDER FUME "STANDARD ATMOSPHERES"	19
5. VARIATIONS IN RESIN ACID COMPOSITION OF SOLDER FUME	20
5.1 Introduction	20
5.2 Effect of Variations in Filter Material	20
5.2.1 Chemical Treatment of Filters	21
5.3 Effect of Variations in Filter Diameter and Sampling Head Type	22
5.3.1 Solder Fume Samples	22
5.3.2 Solvent Extracted Flux Samples	22
5.4 Effect of Variations in Total Resin Acid Concentration	23
5.5 Effect of Variations in Soldering Iron Temperature	24
5.6 Resin Acid Compositions of Various Solder Types and Gauges	26
5.7 Sample Storage	29
5.8 Summary of Results	31
6. PERSONAL SAMPLING METHOD FOR RESIN ACIDS IN SOLDER FUME	32
6.1 Proposed Sampling Method	32
6.2 Filter Pore Size and Sampling Efficiency	32
6.3 Filter Head Experiment	34
6.4 Breathing-Zone versus Lapel Sampling	35
6.5 Sampling Rates	36
6.5.1 Low Flow Rate Samples	36
6.5.2 High Flow Rate Samples	36
6.6 Estimation of Detection Limits	36
6.7 Solder Fume Particle Size	38
7. FIELD TRIALS	40
7.1 Sampling Methods	40
7.1.1 Sample Types	40
7.1.2 Analysis of Filter Samples	40
7.1.3 Analysis of Charcoal Tube Samples	41
7.1.4 Sample Blanks	41
7.2 Field Trial at a Television Repair Facility (I)	41
7.2.1 Filter Samples	41
7.2.2 Charcoal Tube Samples	42

CONTENTS

7.3 Field Trial at a Television Repair Facility (II)	43
7.3.1 Filter Samples	44
7.3.2 Gravimetric Analysis	45
7.3.3 Charcoal Tube Samples	46
7.4 Field Trial at an Electrical Components Manufacturer	46
7.4.1 Filter Samples	48
7.4.2 Gravimetric Analysis	50
7.4.3 Charcoal Tube Samples	51
8. CONCLUSIONS AND RECOMMENDATIONS	52
REFERENCES	54
APPENDICES	56

1. INTRODUCTION AND OBJECTIVES

Fume generated from rosin cored solder is known to cause respiratory problems, although comparatively little is known about the identities of specific causative agents in the fume. Occupational exposure to solder fume is currently measured in terms of aldehyde exposure, defined as a formaldehyde equivalent by colorimetric methods. The Occupational Exposure Standard is 0.1 mg/m^3 of aliphatic aldehydes, expressed as formaldehyde⁽¹⁾, and was originally based on the levels which caused irritation in volunteers who were accustomed to working in solder fume, and has remained unchanged since. However, formaldehyde can be generated from a number of common sources other than solder fume such as tobacco smoke, vehicle emissions and chipboard. Since the formaldehyde levels generated from solder fume are often very low, these alternative sources can lead to erroneous or inaccurate estimates of solder fume exposure being obtained.

Solder fume generated from rosin-cored solder of the type used in the electrical and electronic industries comprises principally diterpene resin acids, volatile mono and sesquiterpenes and other volatile components including aldehydes, as well as other higher aldehydes and anhydrides⁽²⁾. The work described in this report is mainly restricted to an investigation of potential sampling and analytical techniques, since the identification of the various components present has been largely covered in the previous parts. Methods of sampling and analysis for the volatile and in particular the resin acid components of solder fume derived from rosin cored solder have been investigated and developed.

This study was intended to investigate the sampling and analysis of the volatile and resin acid components of solder fume, with the objective of providing a more accurate guide to occupational exposure of solder fume than the present formaldehyde based limit⁽¹⁾. This in turn could lead to an improved Occupational Exposure Standard (OES) and to more appropriate monitoring techniques.

2. GAS CHROMATOGRAPHIC ANALYSIS OF VOLATILE FRACTION

2.1 QUALITATIVE ANALYSIS

Gas chromatographic analysis is used for both the volatile (collected onto charcoal tubes) and particulate (collected onto membrane filters) fractions of the fume. Both are solvent extracted and injected onto the GC as solutions, however the particulate sample also requires methylation before analysis. Initially the analyses carried out were qualitative in order to identify the major components present, but once this had been achieved the samples were analysed quantitatively with the aid of calibration standards. The following paragraphs detail the sample preparation and chromatographic conditions developed for the two types of samples.

After sampling the contents of each charcoal tube are emptied into a 2 ml vial and capped with a screw-top teflon-silicone septum. The sample is then desorbed by adding 0.5 ml of carbon disulphide containing a known concentration of an internal standard (dodecane) and left to stand for 30 minutes. 1 µl injections of the sample solution are then made onto the column using the chromatographic conditions given in Table 1.

TABLE 1: GAS CHROMATOGRAPHIC ANALYSIS CONDITIONS FOR VOLATILES ANALYSIS

Column Type	S.G.E. 12QC3/BP1 0.5
Injector Temperature	250°C
Detector Type	FID
Detector Temperature	300°C
Column Pressure	7 psi
Column Temperature 1	40°C
Time at Temperature 1	5 minutes
Temperature Ramp 1	2°C per minute
Column Temperature 2	60°C
Time at Temperature 2	1 minute
Temperature Ramp 2	25°C per minute
Column Temperature 3	285°C
Time at Temperature 3	0 minutes
Total Run Time	25 minutes

The samples were analysed using a column pressure of 7 psi, as this seems to give adequate separation of the various components. A lower column pressure of 3 psi was tried briefly, but this seemed to offer no improvement in separation whilst increasing the sample run time.

Much of the work of identifying the numerous volatile components present has already been detailed in a previous report using a combination of GC retention times, infra-red spectroscopy and mass spectroscopy⁽³⁾, although the chromatographic conditions used were somewhat different from those in Table 1. All that was therefore required was to obtain the the retention times of the various volatile components under the standard conditions shown above, and this was achieved using sets of prepared standard solutions. The chemical structures of the main volatile components are shown in Appendix I.

2.2 QUANTITATIVE ANALYSIS

Quantitative analysis of the samples was carried out using calibration lines for the major components (toluene, xylene, pinene, limonene and terpinene) prepared in the following way.

Approximately 400 mg of toluene (Rathburn, GDG) was accurately weighed into a 5 ml volumetric flask and made up to volume with carbon disulphide (CS₂). This process was repeated with *p*-xylene (Fisons, RG), *m*-xylene (Fisons, RG), *o*-xylene (Aldrich, 99+%), α -pinene (Fluka, >97%), β -pinene (Aldrich, 98%), limonene (Aldrich, 97%) and α -terpinene (Fluka, 95%). 0.6 ml of each component solution was pipetted into a single 10 ml volumetric flask and the mixture made up to volume with CS₂. 0.5 ml of this solution was then pipetted into a 10 ml volumetric flask and made up to volume with CS₂, giving a solution containing approximately 240 μ g/ml of each component.

A second solution was made up in a similar way but using the following volumes of the component solutions - 0.3 ml toluene, 0.4 ml *p*-xylene, 0.5 ml *m*-xylene, 0.6 ml *o*-xylene, 0.7 ml α -pinene, 0.8 ml β -pinene, 0.9 ml limonene and 1.0 ml α -terpinene.

1 ml of each solution was placed in a vial, and injected onto a 12 m QC3 BP1-0.5 column in a 1 μ l volume using the GC conditions shown in Table 1, giving 2 standards containing from 129 to 415 ng of the various components (see Table 2).

TABLE 2: VOLATILE SOLUTIONS DATA

COMPONENT NAME	FLASK WEIGHT (mg)		COMPONENT WEIGHT (μ g)	COMPONENT CONC. (μ g/ml)	
	BEFORE	AFTER		SOLUTION 1	SOLUTION 2
Toluene	1.08682	1.51635	429.53	257.7	128.9
<i>para</i> -Xylene	1.19853	1.62924	430.71	258.4	172.3
<i>meta</i> -Xylene	2.44234	2.87204	429.70	257.8	214.9
<i>ortho</i> -Xylene	2.07788	2.51352	435.64	261.4	261.4
α -Pinene	1.85559	2.28479	429.20	257.5	300.4
β -Pinene	1.17308	1.59718	424.10	254.5	339.3
Limonene	1.18191	1.59911	417.20	250.3	375.5
γ -Terpinene	1.06486	1.47956	414.70	248.8	414.7

Table 3 summarises the results of the GC analyses giving the retention times of both the main peak for each component along with a calculated calibration line in the form $y = mx$, where y is the peak area and x is the mass injected in ng. Also listed are the retention times of a number of minor peaks associated with the individual main components together with their size relative to the main peak area.

Samples collected onto charcoal tubes were desorbed into carbon disulphide as described in Section 2.1 and a 1 μ l injection made onto the GC. The major components were identified from their retention times and quantity of each injected calculated from their peak areas and the calibration lines quoted in Table 3. The airborne concentration of each component in the sample could then be calculated using the following equation.

$$C_i = (M_i \times V_s) / (V_a \times V_i \times 1000)$$

C_i = Airborne Concentration (mg/m³)

M_i = Mass Injected (ng)

V_s = Volume of Solution (μ l)

V_a = Volume of Air Sample (l)

V_i = Volume of Solution Injected (μ l)

If the concentration is required in ppm the following equation may be used to convert the units.

$$C_2 = (C_1 \times 24.45 \times T) / (MW \times 298)$$

C_2 = Airborne Concentration (ppm)

T = Sampling Temperature (K)

MW = Molecular Weight of Component (g)

TABLE 3: VOLATILE COMPONENTS CHROMATOGRAPHIC DATA

COMPONENT NAME	RETENTION TIME (mins)	CALIBRATION (y = mx)	MINOR PEAKS (RT and Relative Quantity)
Toluene	0.86	194.4x	a) 10.03 minutes (0.7%)
<i>para</i> -Xylene	1.70*	192.8x*	a) 1.60 minutes (0.05%) b) 3.50 minutes (0.25%)
<i>meta</i> -Xylene	1.70*	192.8x*	a) 1.60 minutes (0.05%) b) 3.50 minutes (0.25%)
<i>ortho</i> -Xylene	2.00	191.4x	
α -Pinene	3.00	177.2x	a) 3.25 minutes (1.7%) b) 8.98 minutes (1.0%) c) 9.54 minutes (0.8%) d) 11.30 minutes (0.5%) e) 11.90 minutes (0.8%)
β -Pinene	4.05	186.1x	a) 9.25 minutes (0.4%) b) 15.00 minutes (0.3%)
Limonene	6.33	187.0x	a) 4.90 minutes (2.1%) b) 8.25 minutes (1.5%)
γ -Terpinene	7.80	179.2x	a) 5.85 minutes (2.6%)

* = *para*- and *meta*-xylene were not separated so a combined calibration line for the two components is quoted.

3. GAS CHROMATOGRAPHIC ANALYSIS OF THE PARTICULATE FRACTION

3.1 OPTIMISATION OF SAMPLE PREPARATION METHOD

In order to obtain good quality chromatograms from the resin acids contained in solder fume particulate, it is necessary to methylate the sample before injection onto the GC. Much of the work on particulate samples in this report was carried out using a methylation process developed several years ago⁽³⁾ using N,N-dimethylformamide dimethyl acetal and N,N-dimethylformamide as a solvent. The total volume of each sample has been 0.5 ml, so that each 1 µl injection represents about 1/500th of the total sample volume. In addition a known volume of methyl stearate is added to each sample to act as an internal standard.

However recent examination of the literature^(4,5) has yielded the following information which suggests that the methylation process used above could be improved both in terms of performance and the need to use N,N-dimethylformamide.

- A number of different solvents may be used including pyridine, benzene, alcohols, halogenated hydrocarbons, N,N-dimethylformamide, acetonitrile and tetrahydrofuran.
- Only a 4-6:1 excess of reagent is required.
- The mixture should be protected from contact with air during heating.
- The reaction should be carried out under scrupulously dry conditions since N,N-dimethylformamide dialkyl acetals are moisture-sensitive and hydrolyse to N,N-dimethylformamide and the corresponding alcohol in the presence of water.
- The reaction usually goes to completion immediately on solution of the sample and so heating is only required with samples which do not fully dissolve at room temperature.
- Heating to 50-60°C is sufficient.
- Sterically hindered acids react almost as fast as unhindered acids.

With these observations in mind, the following minor revisions to the methylation process were introduced.

- To use toluene as the solvent instead of N,N-DMF (for the following reasons).
 - a) Toluene is less unpleasant to use than N,N-DMF.
 - b) Toluene is less miscible with water than N,N-DMF so the reaction mixture should remain dryer, making the reagent less prone to hydrolysis.
 - c) Toluene produces a "cleaner" chromatogram than N,N-DMF.
- To reduce the proportion of dimethyl acetal reagent in the reaction mixture from 40% to around 17%, thus reducing the peak size in the chromatogram due to the reagent. In addition, the reagent would be added as a 25% solution in toluene instead of neat.
- To reduce the final volume of each sample from 0.5 to 0.3 ml, thus raising each 1 µl injection to 1/300th of the total sample volume from 1/500th. This in turn should increase the sensitivity of the method by around 60% (all other things being equal).

In addition an experiment was carried out to examine whether the efficiency of the methylation process is reduced by a lack of heating.

3.1.1 Revised Methylation Procedure

The methylating reagent was diluted to a 25% solution by placing 5 ml of N,N-dimethylformamide dimethyl acetal in a 20 ml volumetric flask and making up to volume with toluene. An internal standard solution was made up by accurately weighing around 15 - 20 mg of methyl stearate into a 20 ml volumetric flask and making up to volume with toluene. The sample, as an ethereal solution of around 5 ml, was then blown to dryness in a 2 ml reacti-vial, before adding 0.2 ml of the reagent solution and capping with a teflon-silicone septum. The sample was heated to 60°C for 30 minutes and then allowed to cool to room temperature, before 0.1 ml of the internal standard solution was added (making the final solution volume 300 µl) and swirled gently to mix. Finally, using a glass pipette, the sample was transferred to a 1 ml GC vial for analysis.

3.1.2 Comparison of Methods

A comparison of the proposed methylation process above with the original was carried out using four spiked samples containing an identical quantity of solder extract solution (0.6 ml). The four samples were methylated using the conditions given below with the aim of determining whether the process was adversely affected by a change in solvent to toluene, a lower concentration of methylating reagent or a lack of heating during methylation. For the purposes of this comparison, Samples 2 to 4 were made up to 500 µl with toluene in order that they have the same final volume as the reference Sample 1.

Sample 1 - The sample was methylated in a mixture of 0.2 ml N,N-dimethyl formamide dimethyl acetal and 0.2 ml N,N-dimethyl formamide heated to 60°C for 30 minutes. After heating, an internal standard of methyl stearate in 0.1 ml of N,N-dimethyl formamide was added giving a final solution volume of 500 µl. This is the original methylation method and will be used as the reference.

Sample 2 - The sample was methylated in a mixture of 0.1 ml of a 25% solution of N,N-dimethyl formamide dimethyl acetal in toluene and 0.3 ml toluene heated to 60°C for 30 minutes. After heating an internal standard of methyl stearate in 0.1 ml of N,N-dimethyl formamide was added giving a final solution volume of 500 µl. The main differences from the reference sample above are therefore the decreased content of methylating reagent and the use of toluene rather than N,N-dimethyl formamide as the solvent.

Sample 3 - The sample was methylated in a mixture of 0.2 ml of a 25% solution of N,N-dimethyl formamide dimethyl acetal in toluene and 0.2 ml toluene heated to 60°C for 30 minutes. After heating, an internal standard of methyl stearate in 0.1 ml of N,N-dimethyl formamide was added giving a final solution volume of 500 µl. This sample is similar to Sample 2 above but has a higher content of the methylating reagent.

Sample 4 - The sample was methylated in a mixture of 0.2 ml of a 25% solution of N,N-dimethyl formamide dimethyl acetal in toluene and 0.2 ml toluene left to stand at room temperature for 30 minutes. After standing, an internal standard of methyl stearate in 0.1 ml of N,N-dimethyl formamide was added giving a final solution volume of 500 µl. This sample is similar to Sample 3 above but with no heating during the methylation process.

For each sample an injection of 1 µl was made into the GC using standard column and instrument conditions. Additionally, Sample 4 was re-injected after standing for a further hour at room temperature.

The results of the five injections are shown in Table 4. Samples 1 to 3 are virtually identical, within experimental error, indicating that using toluene as the solvent causes no significant loss in methylation efficiency. The lack of a significant difference between Samples 2 and 3 indicates that a reagent content of around 20% is more than sufficient for the methylation process (particularly as these samples are much more heavily loaded than any air samples are likely to be).

Samples 4 and 5 however, which were not heated during the methylation process, do show significantly reduced TRA peak areas of around 20% when compared with the reference Sample 1. This indicates that heating is important for this particular methylation process, and it is unlikely that this part of the process can be omitted. The lack of any significant difference between Sample 4 and 5 indicates that even a period at room temperature of twice the normal heating period does not compensate for the lack of heat. It may also indicate that the sample is only around 80% soluble without heating.

TABLE 4: COMPARISON OF METHYLATION METHODS

SAMPLE NUMBER	1	2	3	4	5
SOLVENT USED	DMF	Toluene	Toluene	Toluene	Toluene
METHYLATING REAGENT (%)	40	5	10	10	10
HEATING TO 60°C	Yes	Yes	Yes	No	No
STANDING TIME (minutes)	---	---	---	0	60
TOTAL RESIN ACID (ng)*	833	823	859	663	652
TRA AS % OF SAMPLE 1	100.0	98.8	103.1	79.6	78.3

* = Total Resin Acid injected calculated from total peak area on chromatogram.

3.2 OPTIMISATION OF CHROMATOGRAPHIC CONDITIONS

The mixture of resin acids contains a number of very similar compounds, thus if an acceptable separation is to be obtained the chromatographic conditions require a greater degree of optimisation than usual. Ideally, as well as resulting in good separation this process of optimisation should also produce a flat baseline and a short run time.

Previous work on the analysis of resin acids used a combination of a 50 m non-polar BP1 capillary column with a nitrogen carrier gas and a splitless injection⁽²⁾. The long column length was used to obtain reasonable separation of the resin acid components, the nitrogen carrier gas as a consequence of the flow control equipment attached to the GC and the splitless injection from efforts to obtain infra-red spectra from the samples using a fourier transform infra-red (FTIR) detector. This combination however had resulted in large, tailing solvent peaks, a poor quality sloping baseline, only average separation of the resin acid components and a long (30 - 40 minute) run time despite using elevated column temperatures (200 - 300°C). The GC used also required manual injection, which, even with extreme care when injecting the samples showed significant variations in injection volumes (revealed by the use of an internal standard).

The biggest improvement in chromatogram quality came from changing to a split injection using the standard split/splitless injector. This had the effect of reducing peak tailing, particularly on the solvent peak, producing sharper peaks and a much flatter baseline. Several split ratios of between 2 and 10:1 were tried, resulting in an optimum setting of around 3:1 for the best compromise of chromatogram quality with sensitivity. The use of a split mode of injection also had the added attraction, particularly with "dirty" air samples, that any debris in the sample is swept out of the injector to waste rather than down the column, thus reducing the need to clear the column at elevated temperatures after each run, and generally increasing the column life and performance.

The purchase of an improved GC system enabled the use of other carrier gases in place of nitrogen. From the literature⁽¹³⁾ it is apparent that of the three main carrier gases in common use, nitrogen gives the slowest analysis times, hydrogen the fastest and helium something in between. This is because nitrogen has an optimum linear velocity through the column of around 12 cm/s, whereas in the case of hydrogen this is increased to around 40 cm/s. Hydrogen also has a much broader range of velocities over which separating performance is very similar than is the case for nitrogen. The performance of a column in which hydrogen is used as the carrier gas will be within around 10% of optimum within the linear velocity range 30 to 70 cm/s, but for nitrogen only between the linear velocity range 10 to 20 cm/s.

A number of different column pressures were tried with around 7 psi being found to give an analysis time for the resin acids of under 15 minutes. This was found to give a flow rate through the capillary column of around 3 ml/min at a column temperature of 150°C. The total run time for each sample was around 30 minutes allowing for a 10 minute temperature ramp to clear the column of unwanted material and 5 minutes for the column to come back down to the starting temperature and re-equilibrate (this compares with around 60 minutes previously).

The run separation achieved and the total run time are also very dependent on the temperature program used. This was developed largely by trial and error with the aim of achieving the optimum performance at the minimum temperature (for increased column life). The effectiveness of the temperature program was increased by the use of multiple temperature ramps, with the details of the final program given below in Table 5. The program falls into two main parts with the separation and analysis largely achieved in the first 15 minutes, followed by a 10 minute column clearance stage ready for the next sample.

Finally, the introduction of an improved GC system allowed the replacement of manual injection with a computer programmed mechanical auto-injector. This allowed much more accurate and reproducible injections to be made than was possible with the previous manual injector (although an internal standard continues to be used as a check of accuracy). In addition, it also enabled the running of large batches of samples through the GC overnight, thus greatly increasing the rate at which samples could be analysed. For example, in a working day using the manual injector it was possible to analyse only around 8 to 9 samples at maximum, whereas with the auto-injector and the revised method of analysis 25 to 30 samples can be analysed overnight.

TABLE 5: GAS CHROMATOGRAPHIC ANALYSIS CONDITIONS (RESIN ACIDS)

Column Type	S.G.E. 12QC3/BP1 0.5
Injector Temperature	250°C
Detector Type	FID
Detector Temperature	300°C
Column Pressure	7 psi
Column Temperature 1	180°C
Time at Temperature 1	0 minutes
Temperature Ramp 1	1°C per minute
Column Temperature 2	195°C
Time at Temperature 2	0 minutes
Temperature Ramp 2	20°C per minute
Column Temperature 3	285°C
Time at Temperature 3	5.5 minutes
Total Run Time	25 minutes

3.3 QUALITATIVE ANALYSIS

After sampling, the contents of each filter was desorbed into ether and methylated as described earlier in Section 3.1.1. 1 to 2 µl injections of the sample solution were then made onto the column using the chromatographic conditions given above in Table 5. The main resin acid components were identified by a mixture of retention times, infra-red spectroscopy, mass spectroscopy and comparison with chromatograms and spectra in the literature⁽⁸⁻¹²⁾. Chemical structures for the main resin acids are shown in Appendix 2, and further details of the identification procedure in Part III of this series of reports.

3.4 QUANTITATIVE ANALYSIS

Once preliminary identification of the resin acids had been achieved, calibration standards of the two main resin acid components, abietic and dehydroabietic acid, along with the methyl stearate internal standard were prepared for subsequent quantitative analysis of samples. This quantitative method for determining resin acids is based on the relative FID responses of the acids to that of an internal standard of methyl stearate. By using the relative FID response factors between methyl stearate and resin acids the effect of errors caused by changes in the performance of the GC should be reduced.

A set of 42 calibration standards, comprising 14 methyl stearate, 14 abietic acid and 14 dehydroabietic acid, was prepared. Those standards containing resin acids were methylated as described in Section 3.1.1, whilst those containing only methyl stearate were treated in a similar fashion, but with the following differences:

- The standards were not heated during preparation since the stearate is already methylated.
- 0.1 ml of clean stearate-free toluene was added to make up to the final volume of 0.3 ml.

3.4.1 Methyl Stearate Standards

Around 75 mg of methyl stearate (Aldrich, 99%) was accurately weighed into a 10 ml volumetric which was then made up to volume with ether to give a solution of approximately 7.5 mg/ml. This was diluted 10 times and then a further 5 times with ether to give a final solution of approximately 150 µg/ml methyl stearate in ether. 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 ml aliquots of this solution were then taken, evaporated to dryness under a dry air flow and dissolved in 0.2 ml of methylating reagent (Section 3.1.1) and 0.1 ml of toluene. 1 and 1.5 µl injections of each standard plus a blank were injected into the GC using the standard conditions, giving a set of 14 standards with a total resin acid content of 50 to 1500 ng.

The methyl stearate peak areas from each of the standards are given in Table 6. These areas, when plotted against the gravimetrically determined methyl stearate content of the injection give the calibration line $y = 100.509x$ (correlation coefficient, $r = 0.9993$) shown in Figure 1.

FIGURE 1: METHYL STEARATE CALIBRATION LINE

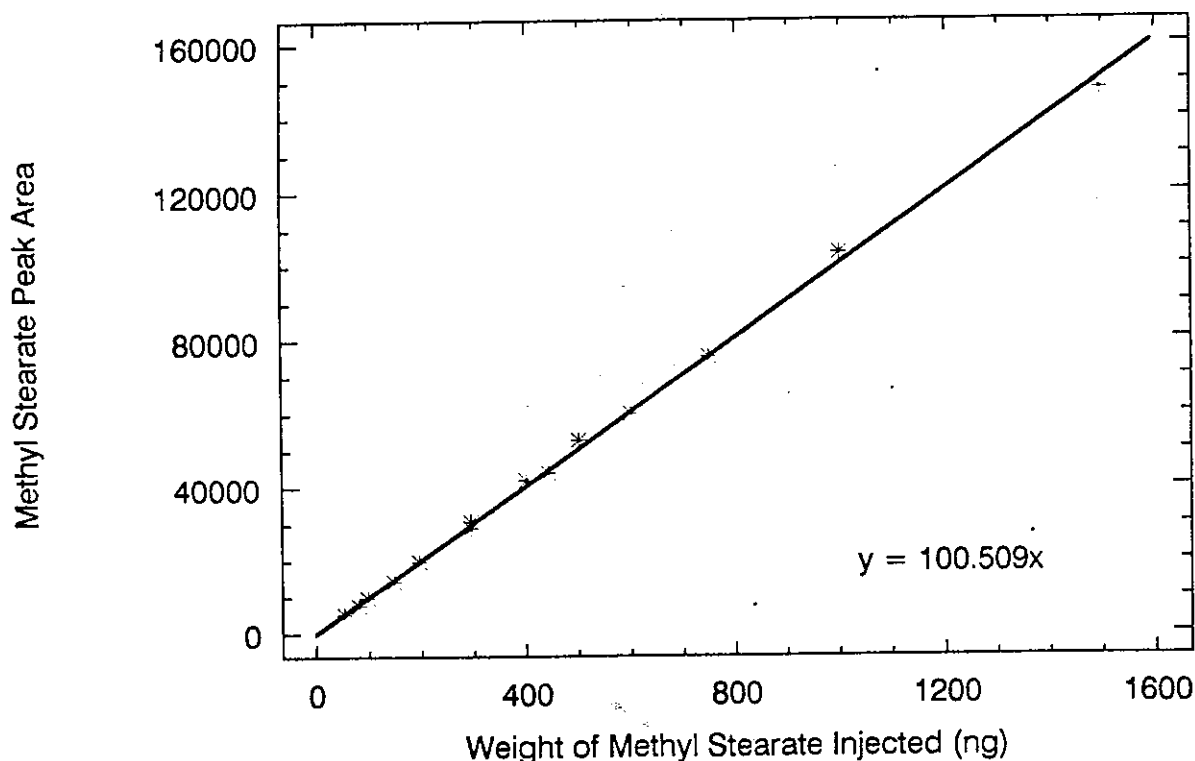


TABLE 6: METHYL STEARATE CALIBRATION STANDARDS

STANDARD NUMBER	INJECTION VOLUME (μ l)	GRAVIMETRIC M/S CONTENT (ng)	M/S PEAK AREA	CALCULATED M/S CONTENT (ng)	DIFFERENCE (%)
1	1.0	53.92	5229	52.02	-3.5
2	1.5	80.88	7663	76.24	-5.7
3	1.0	97.90	9756	97.07	-0.8
4	1.5	146.84	14136	140.65	-4.2
5	1.0	195.66	19726	196.26	+0.3
6	1.5	293.49	28759	286.13	-2.5
7	1.0	294.27	30452	302.98	+3.0
9	1.0	399.36	41627	414.16	+3.7
8	1.5	441.41	43707	434.85	-1.5
11	1.0	499.15	52487	522.22	+4.6
10	1.5	599.05	59829	595.26	-0.6
12	1.5	748.73	75237	748.56	-0.0
13	1.0	998.16	103310	1027.87	+3.0
14	1.5	1497.25	147427	1466.81	-2.0

TABLE 7: ABIETIC ACID CALIBRATION STANDARDS

STANDARD NUMBER	INJECTION VOLUME (μ l)	GRAVIMETRIC TRA CONTENT (ng)	TRA PEAK AREA	CALCULATED TRA CONTENT (ng)	DIFFERENCE (%)
1	1.0	20.08	1472	20.04	-0.2
2	1.5	30.12	2150	29.28	+2.8
3	1.0	40.56	2963	40.34	+0.5
4	1.5	60.83	4310	58.68	+3.5
5	1.0	80.30	5916	80.55	-0.3
6	1.5	120.44	8505	115.79	+3.9
7	1.0	120.86	9373	127.60	-5.6
8	1.0	161.73	12400	168.82	-4.4
9	1.5	181.28	13133	178.80	+1.4
10	1.0	199.87	15694	213.66	-6.9
11	1.5	242.60	17599	239.60	+1.2
12	1.5	299.80	22095	300.80	-0.3
13	1.5	606.52	44346	603.75	+0.5
14	1.5	606.52	44374	604.12	+0.4

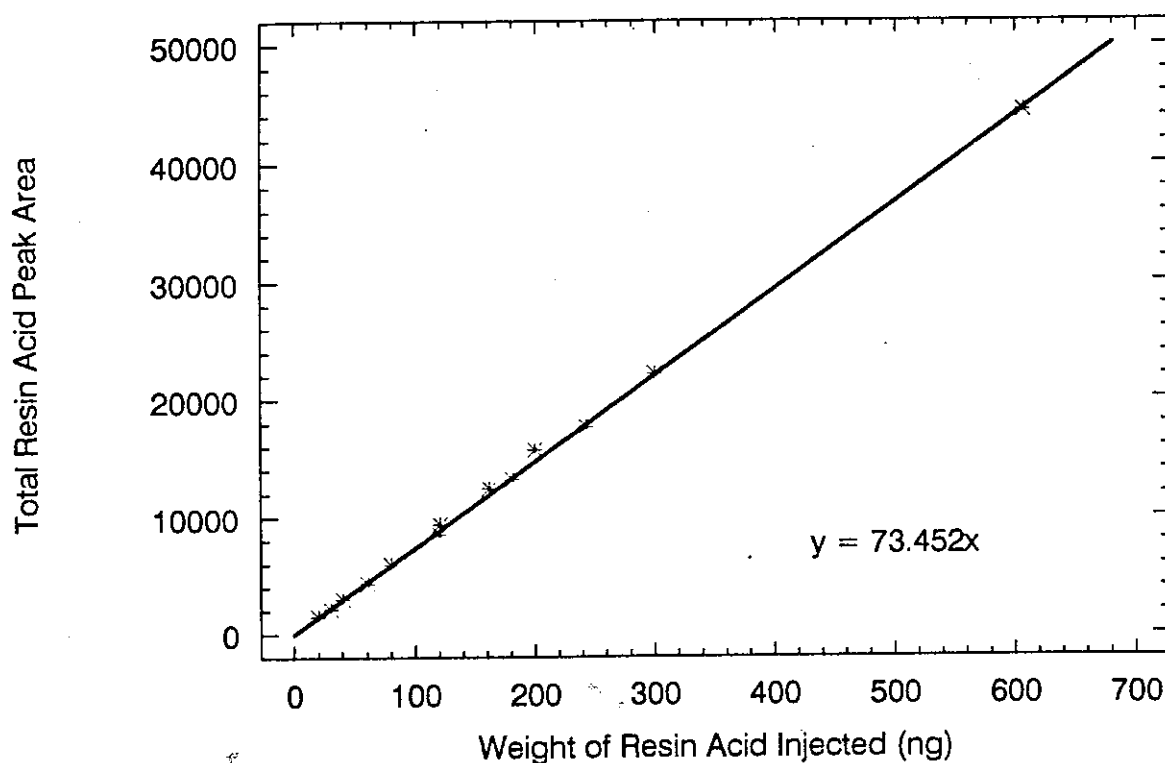
3.4.2 Abietic Acid Standards

Around 60 mg of abietic acid (Fluka, >97%) was accurately weighed out into a 10 ml volumetric which was then made up to volume with ether to give a solution of approximately 6 mg/ml. This was diluted 10 times and then a further 10 times with ether to give a final solution of approximately 60 µg/ml abietic acid in ether. 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 ml aliquots of this solution were then taken, evaporated to dryness under a dry air flow and methylated as described in Section 3.1.1. 1 and 1.5 µl injections of each standard plus a blank were injected into the GC using the standard conditions, giving a set of 14 standards with a total resin acid content of 20 to 600 ng. Measurement of the peak areas for the eight main resin acids indicated the abietic acid to comprise around 75 - 80% of the total resin acid content of the standard. This estimate is made on the assumption that all eight resin acids have a similar FID response (see Section 3.4.4).

The total resin acid peak areas from each of the standards are given in Table 7. These areas, when plotted against the gravimetrically determined total resin acid content of the injection give the calibration line $y = 73.452x$ (correlation coefficient, $r = 0.9996$) shown in Figure 2.

Total resin acid peak area is used for the calibration because the "abietic acid" standards contain significant quantities of other resin acids, and consequently plotting abietic acid peak area alone against the gravimetric determined resin acid content would not give a true FID response. Also, if the assumption that all resin acids have a similar FID response is correct, the slope of the calibration line obtained using total resin acid peak area should be roughly constant whatever the resin acid composition of the standards.

FIGURE 2: ABIETIC ACID CALIBRATION LINE



3.4.3 Dehydroabietic Acid Standards

Around 60 mg of dehydroabietic acid (Pfaltz & Bauer, Tech.) was accurately weighed out into a 10 ml volumetric which was then made up to volume with ether to give a solution of approximately 6 mg/ml. This was diluted 10 times and then a further 10 times with ether to give a final solution of approximately 60 µg/ml dehydroabietic acid in ether. 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 ml aliquots of this solution were then taken, blown to dryness and worked up as described in Section 3.1.1. 1 and 1.5 µl injections of each standard plus a blank were injected into the GC using the standard conditions, giving a set of 14 standards with a total resin acid content of 20 to 600 ng. GC analysis of the standards showed them to be around 65 - 70% dehydroabietic acid, based on measurement of the relative peak area of dehydroabietic acid with that for total resin acid.

The total resin acid peak areas from each of the standards are given in Table 8. These areas, when plotted against the gravimetrically determined total resin acid content of the injection give the calibration line $y = 73.280x$ (correlation coefficient, $r = 0.9989$) shown in Figure 3.

TABLE 8: DEHYDROABIETIC ACID CALIBRATION STANDARDS

STANDARD NUMBER	INJECTION VOLUME (µl)	GRAVIMETRIC TRA CONTENT (ng)	TRA PEAK AREA	CALCULATED TRA CONTENT (ng)	DIFFERENCE (%)
1	1.0	18.46	1371	18.72	- 1.4
2	1.5	27.69	2009	27.42	+ 1.0
3	1.0	37.15	2668	36.41	+ 2.0
4	1.5	55.73	3847	52.50	+ 5.8
5	1.0	75.88	5580	76.14	- 0.3
6	1.5	113.83	8016	109.39	+ 3.9
7	1.0	115.73	8378	114.33	+ 1.2
8	1.0	154.10	11478	156.63	- 1.6
9	1.5	173.59	11989	163.61	+ 5.8
10	1.0	193.40	15017	204.93	- 6.0
11	1.5	231.16	16342	223.00	+ 3.5
12	1.5	290.10	20965	286.10	+ 1.4
13	1.0	384.25	29443	401.79	- 4.6
14	1.5	576.38	41764	569.92	+ 1.1

3.4.4 Combination of Standards

The calibration line slopes obtained from the two sets of standards, one predominantly abietic acid and the other predominantly dehydroabietic acid are virtually identical. These results suggest that the main resin acids do indeed have similar FID responses, an observation which is supported by work carried out by other researchers^(15,16). Since preparation of individual calibration lines for all the resin acids would be both costly and time consuming, it was proposed that the results from the abietic and dehydroabietic acid standards be combined to obtain a single calibration line, and to make the assumption that this line is valid for all the main resin acids.

Such a combination of abietic and dehydroabietic acid standards produces the calibration line $y = 73.380x$ (correlation coefficient, $r = 0.9993$) shown in Figure 4.

FIGURE 3: DEHYDROABIETIC ACID CALIBRATION LINE

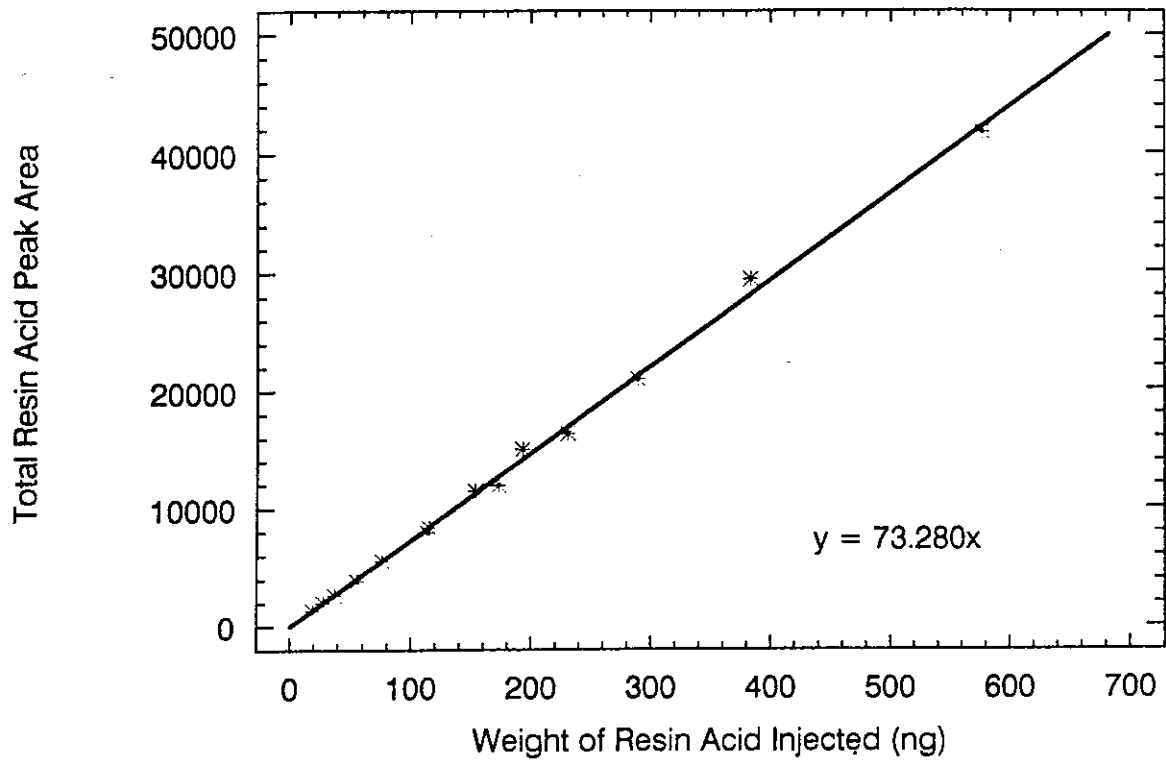
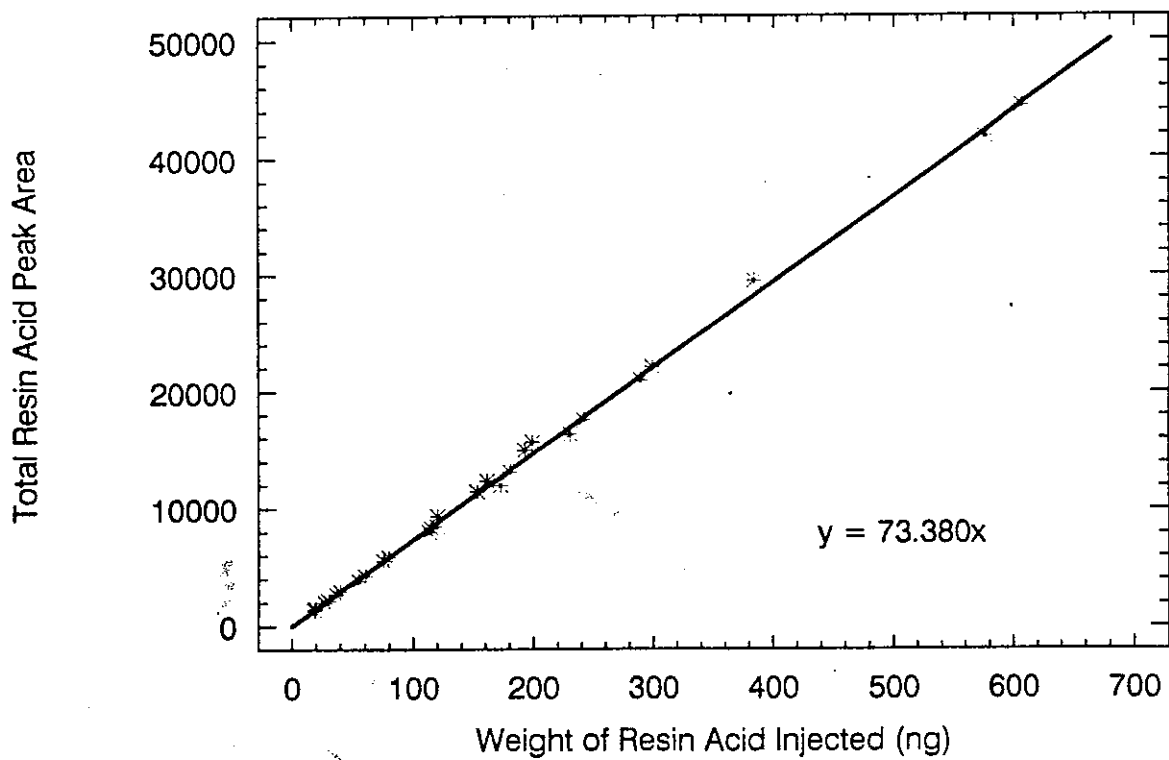


FIGURE 4: COMBINED RESIN ACID CALIBRATION LINE



3.4.5 Relative FID Response Factors

FID Area Response Factor for Resin Acid Methyl Esters = 73.380 per ng injected.

FID Area Response Factor for Methyl Stearate = 100.509 per ng injected.

Relative Area Response Factor = $100.509/73.380 = 1.3697$.

This figure can therefore be used to determine quantitatively the various resin acids present in a given sample if methyl stearate is present as an internal standard.

4. GENERATION OF SOLDER FUME "STANDARD ATMOSPHERES"

Initially, laboratory solder fume samples were deposited on membrane filters using the following method.

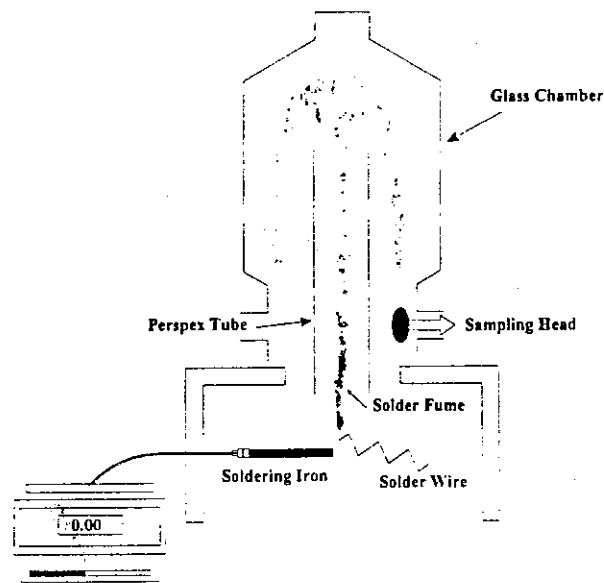
- a) Place the sample filter in the appropriate (13, 25 or 37 mm) filter head.
- b) Mount the filter head on a retort stand in the fume cupboard.
- c) Attach the filter head to a sampling pump and adjust to the desired sampling rate (typically 1 l/min).
- d) Heat a length of solder (typically around 10 cm) at a soldering iron tip held adjacent to the filter head (this process should be carried out at such a rate that the length of solder is used up over a period of around 5 minutes).
- e) Leave the sampling pump running for a further 5 minutes.

This method is simple, but slow, since only one sample is prepared at a time. Also, it is extremely difficult to get a number of similarly loaded sample filters, even using identical lengths of solder and sampling times.

These difficulties led to the development of an alternative method for the preparation of solder fume atmospheres in the laboratory. The main problem with generating solder fume "standard atmospheres" is that much of the fume is present as a particulate, and it is thus not possible to use the equipment used for generating vapour atmospheres⁽¹³⁾. However, the standard atmosphere chamber itself can be modified as shown in Figure 5 to allow generation of reasonably uniform atmospheres of solder fume. The chamber is stoppered at the top, and placed on its stand with the bottom left open. Inside the chamber a circular perspex tube (ca. 10 cm O/D by 40 cm length) is mounted vertically with its end emerging from the bottom of the chamber. Samplers are mounted in the six sampling ports around the base of the chamber (each port can accommodate one 25 mm filter head or two 13 mm filter heads) and set to sample at the desired flow rate. A length of solder (typically ca. 10 cm) is then heated at a soldering iron tip located at the bottom end of the plastic tubing. The warm air carries the solder fume up the inside of the plastic tube and it then falls back down the outside to where the sampling heads are located, and is subsequently drawn onto the sample filters. Since the sample chamber is reasonably symmetrical, the solder fume concentration present at each of the sampling ports is fairly uniform, and this technique allows the preparation of up to 12 similarly fume laden sample filters in the time previously taken to prepare just one (although there is still some batch-to-batch concentration variation).

This method of preparation has been used for the laboratory generated solder samples used in subsequent sections of this investigation.

FIGURE 5: EQUIPMENT FOR GENERATING SOLDER FUME "STANDARD ATMOSPHERES"



5. VARIATIONS IN RESIN ACID COMPOSITION OF SOLDER FUME.

5.1 INTRODUCTION

When sampling solder fume onto membrane filters it was noticed that the composition of the fume tended to change with the length of the sampling time. In particular, the content of abietic acid and palustric acid reduced over longer sampling periods, whilst pinonic and dehydroabietic acid seemed to remain roughly constant. At this stage it was not clear by what process abietic was being lost, or what the products of the decomposition were, although a brief literature review suggested that oxidation was the most likely cause of the changes in composition. A brief summary of four possible oxidation mechanisms outlined in the literature is given in Appendix 3.

Since the main aim of this investigation is the measurement of abietic acid and/or total resin acids, it would be desirable if the sampling method being developed prevented such losses or at least reduced them to a minimum. To this end, Sections 5.2 to 5.7 detail the effects of variables such as filter type, filter diameter, soldering iron temperature, etc on the final resin acid composition, and in particular on abietic acid.

In subsequent sections of this report the following abbreviations are used:

ABI = Abietic Acid

DHA = Dehydroabietic Acid

TRA = Total Resin Acid

5.2 EFFECT OF VARIATIONS IN FILTER MATERIAL

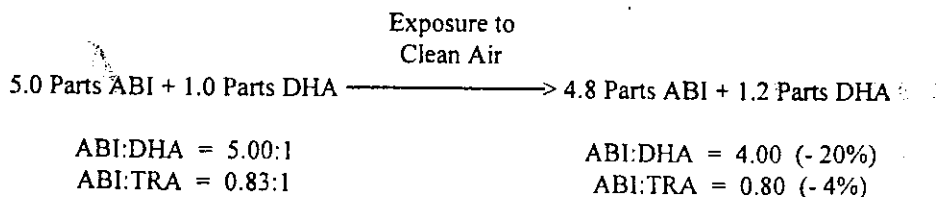
The objective of this experiment was to investigate whether changing the material from which the sampling filters are constructed affects the variations in resin acid composition with sampling time. The filter materials investigated were cellulose nitrate-acetate (Millipore MF), polyvinyl chloride-acrylonitrile (DM800) and teflon (PTFE).

Four Millipore-MF RAWP, four DM800 and four PTFE filters (all 13 mm diameter) were used to collect samples of solder fume generated at around 300°C in the standard atmosphere chamber (see Section 4). One of each type of loaded filter was then used to sample clean air at 1 l/min for 0, 60, 120 and 360 minutes before extraction, methylation and analysis using the standard procedure. This simulates collection of a sample early in a sampling period and will show what happens on subsequent exposure to "clean" air.

The results in Table 9 show that the ABI:DHA ratio falls by around 13, 25 and 12% respectively for the three filter types over the six hour period. The percentage of (ABI + DHA) however, remains almost constant at around 60 - 62% for all three filter types over the same period. This suggests that ABI is being transformed into DHA, and would explain why previous experiments have shown no significant weight loss during prolonged exposure to clean air.

Previously it had been thought that the quantity of dehydroabietic acid in the sample remained constant, and therefore the losses of abietic acid had been quantified by quoting the percentage fall in the ABI:DHA ratio. However, if the lost abietic acid is in fact being converted to dehydroabietic acid, the change in the ABI:DHA ratio will tend to exaggerate the losses of abietic acid as shown in the following example.

A resin acid sample collected onto a filter contains a quantity of resin acid made up of 5 parts abietic and 1 part dehydroabietic. After a period of exposure to clean air the quantity of resin acid on the filter remains the same, but 0.2 parts of abietic have been converted into 0.2 parts of dehydroabietic. This means that the sample is now 4.8 parts abietic and 1.2 parts dehydroabietic, which results in the ABI:DHA ratio falling from 5.0:1 to 4.0:1, a decrease of some 20%. However, this factor exaggerates the losses of abietic since its proportion has in fact fallen by just 4% from 0.83 to 0.80.



The results from this example closely mirror those shown in Table 9, where quite large falls in the ABI:DHA ratio (up to 26%) disguise much more modest falls in abietic content. With the Millipore-MF and PTFE filters, over a 360 minute period sampling clean air the ABI:DHA ratio falls by around 12%, however the abietic content of the sample falls by only around 2%. With the DM800 filters the ABI:DHA ratio falls by around 25%, making the losses of abietic appear quite significant, although the fall is in fact a much less significant 8%.

Whilst these results do not alter the observation that using Millipore-MF and PTFE filters reduces the losses of abietic acid when compared with DM800 filters, they do show that the fall in abietic content of all the samples is far less significant than had previously been thought. It is however recommended that for long term sampling periods (> 2 hour), Millipore-MF filters are used since they offer greater sample stability than the DM800's, whilst being easier to handle and available at lower cost than PTFE. For shorter sampling periods (< 2 hour), either DM800 or Millipore-MF filters can be used as there is no significant difference in sample stability on the two filter materials up to this point.

TABLE 9: EFFECT OF FILTER MATERIAL ON SAMPLING.

Filter Type	Time (mins)	ABI:DHA	Change (%)	DHA:TRA	ABI:TRA	Change (%)	D+A:TRA	Change (%)
RAWP	0	4.110	0.0	0.119	0.490	0.0	0.609	0.0
	60	3.971	-3.4	0.123	0.489	-0.2	0.612	+0.5
	120	3.705	-9.9	0.129	0.479	-2.2	0.608	-0.2
	360	3.587	-12.7	0.134	0.481	-1.8	0.615	+1.0
DM800	0	4.088	0.0	0.120	0.490	0.0	0.610	0.0
	60	3.810	-6.8	0.128	0.489	-0.2	0.617	+1.1
	120	3.488	-14.7	0.137	0.478	-2.4	0.615	+0.8
	360	3.035	-25.8	0.148	0.450	-8.2	0.598	-2.0
PTFE	0	4.146	0.0	0.117	0.485	0.0	0.602	0.0
	60	3.945	-4.8	0.124	0.489	+0.8	0.612	+1.8
	120	3.656	-11.8	0.131	0.481	-0.8	0.612	+1.7
	360	3.657	-11.8	0.129	0.473	-2.5	0.602	0.0

5.2.1 Chemical Treatment of Filters.

A number of washing/chemical treatments were tried on DM800 and Whatman #3 filters, but none appeared to help reduce the on-filter decomposition of abietic acid during sampling. Indeed one or two of the treatments had some fairly undesirable effects on the sampling procedure, with either extra peaks present on the chromatograms (butylated hydroxytoluene) or a drastic reduction in sampling efficiency (potassium hydroxide). The treatments tried included the following.

- Acid washing filters with glacial acetic acid.
- Treating filters with a solution of sodium acetate.
- Treating filters with a solution of ammonium acetate.
- Using filters impregnated with lead acetate.
- Treating filters with butylated hydroxytoluene (an anti-oxidant).
- Treating filters with 4,4-sulphonyldiphenol (an anti-oxidant).
- Treating filters with potassium hydroxide (with the aim of converting the resin acids into potassium salts on the filter).
- Treating filters with a combination of 4,4-sulphonyldiphenol and glycerol (a humectant).
- Silanising filters with a 2% solution of dimethyldichlorosilane in 1,1,1-trichloroethane.

- Combination of silanising filters and washing with glacial acetic acid.

As well as the treatments above, a comparison of samples taken in daylight with those taken in the dark was also made to see if on-filter decomposition of abietic acid was inhibited by a lack of light. However, there was no evidence that keeping the filter in the dark had any beneficial effect on the retention of abietic acid over a 270 minute sampling period.

5.3 EFFECT OF VARIATIONS IN FILTER DIAMETER AND SAMPLING HEAD TYPE

5.3.1 Solder Fume Samples.

This experiment was to investigate whether changes to the filter diameter and design of sampling head affect the stability of resin acid samples deposited on the filter material. The filter diameters compared were 13 mm and 25 mm. The 13 mm filters were mounted in semi-enclosed Millipore filter heads⁽¹⁴⁾ and the 25 mm filters in open Gelman heads. It is important to know in particular if there is any significant loss of performance when using the smaller 13 mm filters since their more compact size makes them preferable for use in personal sampling.

Seven 13 mm and seven 25 mm Whatman #3 filters were exposed to solder fume generated at around 300°C in the standard atmosphere chamber (see Section 4). Loaded filters of each size were used to sample clean air at 1 l/min for 0, 64, 123, 180, 240, 300 and 372 minutes before extraction, methylation and analysis using the standard procedure.

Table 10 indicates that there is no significant difference in sample stability between the two filter sizes. Over a 6 hour sampling period the abietic acid content of the samples falls by around 2.2%/hour for the 13 mm filters and 2.3%/hour for the 25 mm. The ABI:DHA ratio for the two filter sizes decreases by around 6.4%/hour (13 mm) and 8.1%/hour (25 mm). As has been observed in previous experiments, the proportion of abietic and dehydroabietic acid combined remained fairly constant at around 60 - 61%.

The conclusion from this set of experiments is that either filter size can be used for sampling of solder fume without significant effect on the results obtained.

TABLE 10: 13 mm & 25 mm WHATMAN #3 FILTER RESULTS (RESIN ACIDS).

FILTER SIZE	TIME (mins)	ABI:DHA	CHANGE (%)	DHA:TRA	ABI:TRA	CHANGE (%)	D+A:TRA	CHANGE (%)
13	0	3.284	0.0	0.143	0.469	0.0	0.612	0.0
	64	3.010	-8.3	0.151	0.454	-3.2	0.605	-1.2
	123	2.875	-12.5	0.156	0.449	-4.3	0.605	-1.2
	180	2.801	-14.7	0.160	0.448	-4.5	0.608	-0.7
	240	2.731	-16.8	0.164	0.449	-4.4	0.613	+0.1
	300	2.911	-11.4	0.153	0.446	-5.0	0.599	-2.2
	372	2.692	-18.0	0.163	0.438	-6.6	0.601	-1.9
25	0	3.296	0.0	0.140	0.461	0.0	0.601	0.0
	64	2.899	-12.0	0.155	0.448	-2.7	0.603	+0.4
	123	2.824	-14.3	0.156	0.440	-4.5	0.596	-0.8
	180	2.795	-15.2	0.158	0.443	-4.0	0.601	0.0
	240	2.532	-23.2	0.170	0.430	-6.7	0.600	-0.1
	300	2.896	-12.1	0.155	0.449	-2.5	0.605	+0.7
	372	2.411	-26.9	0.175	0.422	-8.4	0.597	-0.6

5.3.2 Solvent Extracted Flux Samples.

The results in Table 10 indicate no significant difference in performance between 13 and 25 mm filter samplers. However, to further test this observation a second set of filters spiked with a solution of solder flux extract instead of

solder fume was analysed. The reason for this change is that resin acid particles deposited on a filter from solution are likely to be much finer than those deposited from solder fume. This should result in the resin acids from solution being more likely to react/oxidise due to their greater surface area, leading to an exaggeration of any differences there may be in sample stability between the two filter sizes.

Seven 13 mm and seven 25 mm Whatman #3 filters were spiked with 200 µl of 18 SWG solder extract solution, and loaded into the appropriate filter holder to draw air at 1 l/min. The filters were then left sampling "clean" air for between 0 and 307 minutes before extraction, methylation and analysis in the usual way.

The results given in Table 11 show that over a 5 hour sampling period, the abietic acid content of the samples falls by an average of 1.3%/hour on 13 mm filters and 2.4%/hour on 25 mm filters. The ABI:DHA ratio for the two filter sizes decreases by approximately 10%/hour (13 mm) and 16%/hour (25 mm). The combined abietic and dehydroabietic acid content again remains fairly constant, although at 70 - 71% for the 13 mm filters and 67 - 68% for the 25 mm filters, a level which is some 8 to 10% above that observed in the fume generated samples (see Section 5.3.1). The reason for this difference may be heat induced isomerisation of abietic acid in the fume samples. Various references in the literature^(15,16) have observed that at temperatures above 200°C abietic acid isomerises to 81% abietic acid, 14% palustric acid and 5% neoabietic acid. Such isomerisation of abietic acid would reduce its proportion from 60% in unheated flux to 49% when heated, a drop of around 11%. This figure is very similar to the 8 - 10% observed in the samples above, indicating an isomerisation process similar to that described above may well be occurring.

The solution spiked filters used in this set of experiments show some differences in sample stability between the two filter sizes, with the 13 mm filters showing smaller losses of abietic acid than 25 mm filters loaded with a similar quantity of resin acids. Whilst these results would appear to suggest that the use of 13 mm filters be recommended, of more relevance is the fact that when loaded with fume (rather than flux solution) no significant difference was observed between the two filter sizes. So the conclusion from these experiments remains that either 13 or 25 mm filters can be used for sampling solder fume without significantly affecting the results.

TABLE 11: SOLDER EXTRACT SPIKED STANDARD SOLUTIONS.

FILTER SIZE	TIME (mins)	ABI:DHA	CHANGE (%)	DHA:TRA	ABI:TRA	CHANGE (%)	D+A:TRA	CHANGE (%)
13	0	5.715	0.0	0.106	0.606	0.0	0.712	0.0
	48	5.222	- 8.6	0.114	0.596	- 1.7	0.710	- 0.3
	100	5.093	- 10.9	0.115	0.586	- 3.2	0.701	- 1.5
	150	4.346	- 24.0	0.130	0.564	- 6.9	0.694	- 2.5
	203	4.846	- 20.5	0.122	0.591	- 2.6	0.713	+ 0.1
	254	4.934	- 13.7	0.118	0.583	- 3.9	0.701	- 1.5
	307	4.265	- 25.4	0.135	0.575	- 5.2	0.710	- 0.3
25	0	5.599	0.0	0.102	0.574	0.0	0.676	0.0
	48	4.625	- 17.4	0.123	0.571	- 0.4	0.694	+ 2.7
	100	4.229	- 24.5	0.127	0.539	- 6.0	0.666	- 1.5
	150	3.992	- 28.7	0.133	0.530	- 7.6	0.663	- 1.9
	203	4.322	- 22.8	0.128	0.552	- 3.8	0.680	+ 0.6
	254	3.979	- 28.9	0.135	0.536	- 6.5	0.671	- 0.7
	307	2.674	- 52.2	0.176	0.471	- 18.0	0.647	- 4.3

5.4 EFFECT OF VARIATIONS IN TOTAL RESIN ACID CONCENTRATION

This experiment investigated whether the resin acid composition of a sample is affected by total resin acid concentration. It was thought that the resin acid composition in the final solution might be concentration dependent because of the need to blow the samples down to dryness during the work-up procedure. If abietic acid is subject to air reaction/oxidation it is possible that this solvent removal process might tend to affect lower concentration samples more significantly than higher concentration ones.

A sample of 18 SWG solder was therefore extracted into ether and used to prepare a set of standards containing 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.3, 1.6 and 2.0 ml aliquots of the extract solution. The 10 standards were then blown down to dryness and analysed in the usual way, with the analyses indicating a concentration range of roughly 0 - 800 ng/ μ l (this range is far in excess of that likely to be encountered in "real" samples).

The results in Table 12 indicate a 1 - 2% rise in the proportion of abietic acid present over a concentration range of aro. rd 40 - 800 ng/ μ l, accompanied by a 1 - 1.5% fall in the proportion of dehydroabietic acid. Such variations are probably well within experimental error and can therefore be regarded as not significant. These variations, although small, do result in a 20% rise in the ABI:DHA ratio which only serves to illustrate how this ratio tends to exaggerate small (and probably insignificant) compositional variations.

The combined proportion of abietic and dehydroabietic acid remains at around 69% over the whole concentration range, a figure which is very similar to that observed in the solution samples in Section 5.3.2, and is once again some 8 - 10% above the levels typically found in fume generated samples (Section 5.3.1).

The conclusion from this experiment is that over a concentration range well in excess of that likely to be encountered in "real" samples, the resin acid composition shows no concentration dependence.

TABLE 12: EFFECT OF VARIATIONS IN TOTAL RESIN ACID CONCENTRATION.

EXTRACT SOLUTION (ml)	ABI:DHA	CHANGE (%)	DHA:TRA	ABI:TRA	CHANGE (%)	D+A:TRA	CHANGE (%)
0.0	---	---	---	---	---	---	---
0.1	5.494	0.0	0.107	0.588	0.0	0.695	0.0
0.2	5.681	+ 3.4	0.103	0.586	- 0.3	0.689	- 0.8
0.4	5.791	+ 5.4	0.101	0.585	- 0.5	0.686	- 1.3
0.6	5.952	+ 8.3	0.099	0.588	0.0	0.687	- 1.2
0.8	6.148	+ 11.9	0.096	0.591	+ 0.6	0.688	- 1.1
1.0	6.220	+ 13.2	0.095	0.592	+ 0.8	0.688	- 1.0
1.3	6.258	+ 13.9	0.095	0.593	+ 0.8	0.687	- 1.1
1.6	6.416	+ 16.8	0.093	0.594	+ 1.1	0.687	- 1.2
2.0	6.568	+ 19.5	0.091	0.598	+ 1.8	0.689	- 0.8

5.5 EFFECT OF VARIATIONS IN SOLDERING IRON TEMPERATURE

Previous experiments in Section 5 have already suggested that there is a change in resin acid composition between fume from solder flux which has been subjected to heat and flux which has remained unheated. It is therefore also possible that the composition of the fume generated from heated solder flux may vary with the temperature to which it is heated. In order to examine the effect of soldering iron temperature on the resin acid composition of the evolved fume therefore, the following experiment was carried out.

Three 13 mm Millipore-MF filters were exposed to fume generated at temperatures between 200 and 400°C from 18 SWG solder in the standard atmosphere chamber. This temperature range roughly covers that of soldering irons encountered during previous factory visits⁽⁶⁾. In order to try and mimic the conditions during "real" soldering, a small soldering iron was used in conjunction with a rapid heating technique. In each case an identical 10 cm length of 18 SWG solder wire was used, with the filters sampling the generated fume at 1 l/min over a period of about 10 minutes. After sampling, the filters were solvent extracted, methylated and analysed using the standard procedure.

At the end of each sampling period the solder source was removed and the three filters taken out of the chamber for analysis in the usual manner. Two 1 μ l injections of each sample were analysed, giving a total of six injections at each temperature setting. To reduce the chance of systematic errors occurring, the experiments were carried out in a random order with respect to temperature.

The results given in Table 13 seem to show no obvious relationship between soldering temperature and the proportion of abietic and dehydroabietic acid, although above 400°C the proportion of abietic acid does begin to fall and dehydroabietic to rise. The combined content of abietic and dehydroabietic acid falls linearly by around 3% over the 210 - 405°C temperature range, however this is probably not significant since it is within typical levels of experimental error.

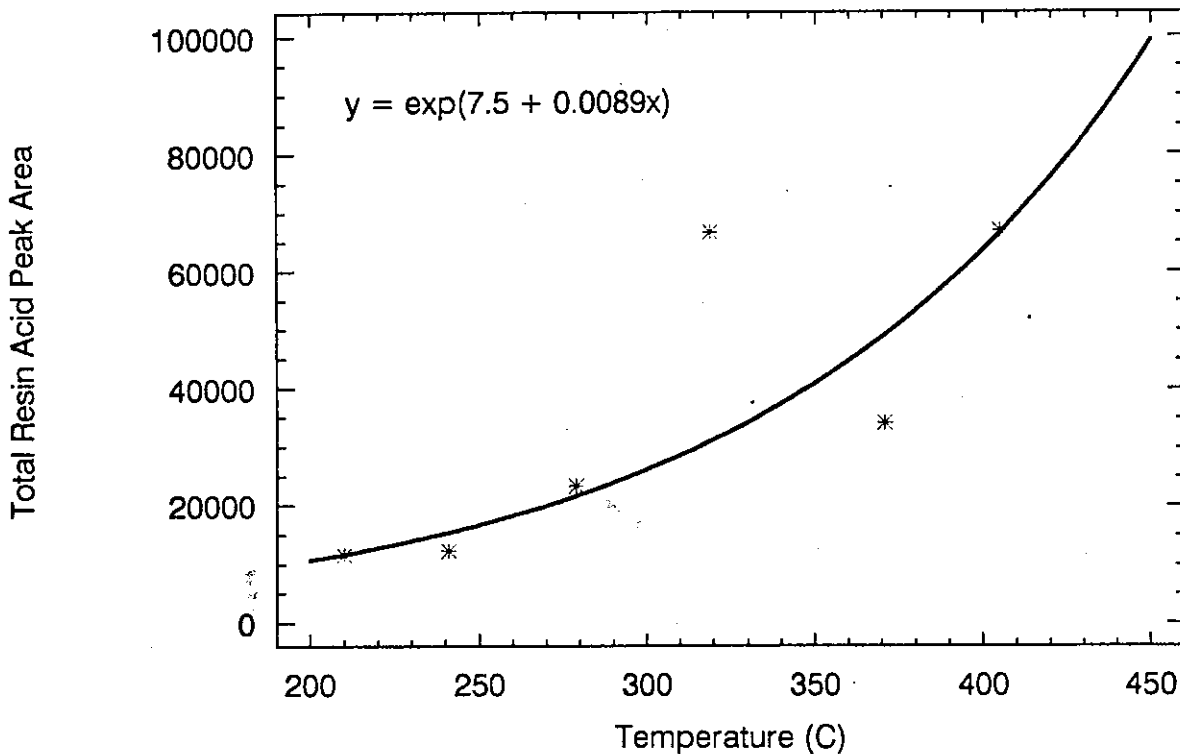
TABLE 13: EFFECT OF VARYING SOLDERING IRON TEMPERATURE.

FILTER TYPE	TEMP. (°C)	ABI:DHA	CHANGE (%)	DHA:TRA	ABI:TRA	CHANGE (%)	D+A:TRA	CHANGE (%)
RAWP	210	4.423	0.0	0.115	0.507	0.0	0.622	0.0
	241	4.866	+ 10.0	0.106	0.515	+ 1.6	0.621	- 0.2
	279	4.711	+ 6.5	0.108	0.507	0.0	0.615	- 1.1
	319	4.468	+ 1.0	0.112	0.498	- 1.8	0.610	- 1.9
	371	4.227	- 4.4	0.116	0.492	- 3.0	0.608	- 2.3
	405	3.600	- 18.6	0.131	0.470	- 7.3	0.601	- 3.4

All the resin acid ratios quoted in Table 13 are the mean of 6 injections from 3 independent filter samples.

Figure 6 illustrates the relationship between soldering iron temperature and the quantity of fume produced (measured as total resin acid peak area). The plot shows that, with one exception, the higher the soldering iron temperature the higher the resin acid peak area, and hence the greater the quantity of fume generated from the solder flux. Figure 6 shows that this temperature dependence of airborne resin acid concentration can be made to fit an exponential regression curve with a best-fit line of $y = \exp(7.5 + 0.0089x)$, where y is the total resin acid peak area and x is the soldering iron temperature.

FIGURE 6: VARIATION OF TRA PEAK AREA WITH SOLDERING IRON TEMPERATURE.



The Multicore product information leaflet on X-32 cored solder⁽¹⁷⁾ also shows increasing fume levels from rosin cored solder with increasing soldering iron temperature. The data is reproduced in Table 14, and shows the amount of fume produced from an unspecified rosin cored solder as % weight loss at 260, 315, 371 and 427°C (500, 600, 700 and 800°F).

TABLE 14: TEMPERATURE DEPENDENCE OF SOLDER FUME LEVELS

SOLDERING IRON TEMPERATURE (°C)	MULTICORE DATA SOLDER FUME (% WEIGHT LOSS)	EXPERIMENTAL DATA SOLDER FUME (DHA PEAK AREA)
260	0.20	17526
315	0.50	28584
371	0.90	47036
427	1.82	77400

Using the best-fit equation above, the theoretical total resin acid peak areas generated from a 10 cm length of 18 SWG solder at these four temperatures can be calculated. These figures are also given in Table 14, and assuming that these total resin acid peak areas are directly proportional to the quantity of fume produced, the temperature dependence of the fume concentration in these experiments can now be compared with that given in the Multicore literature.

Such a comparison shows that in both cases reducing the temperature of the soldering iron tip significantly reduces the quantity of solder fume generated. Savbit 18 SWG solder, which has been used throughout these laboratory experiments, has a minimum recommended soldering temperature is 275°C. Figure 7 illustrates the difference between fume levels at temperatures from 260 to 427°C with that produced at the minimum recommended soldering temperature of 275°C. Figure 8 shows a similar comparison with the fume levels produced by solder at 300°C, a temperature which seems more than sufficient for this type of solder.

Most of the operatives wearing the personal samplers on factory visits carried out in 1989 were using similar 60/40 rosin cored solders⁽⁶⁾. These have a minimum soldering temperature of 275°C, however the mean soldering iron temperature was around 350°C. Figures 7 and 8 suggest that such iron temperatures will generate some 90 to 180% more fume than at the minimum recommended soldering temperature of 275°C, and some 60 to 100% more fume than at a reasonable working temperature of 300°C.

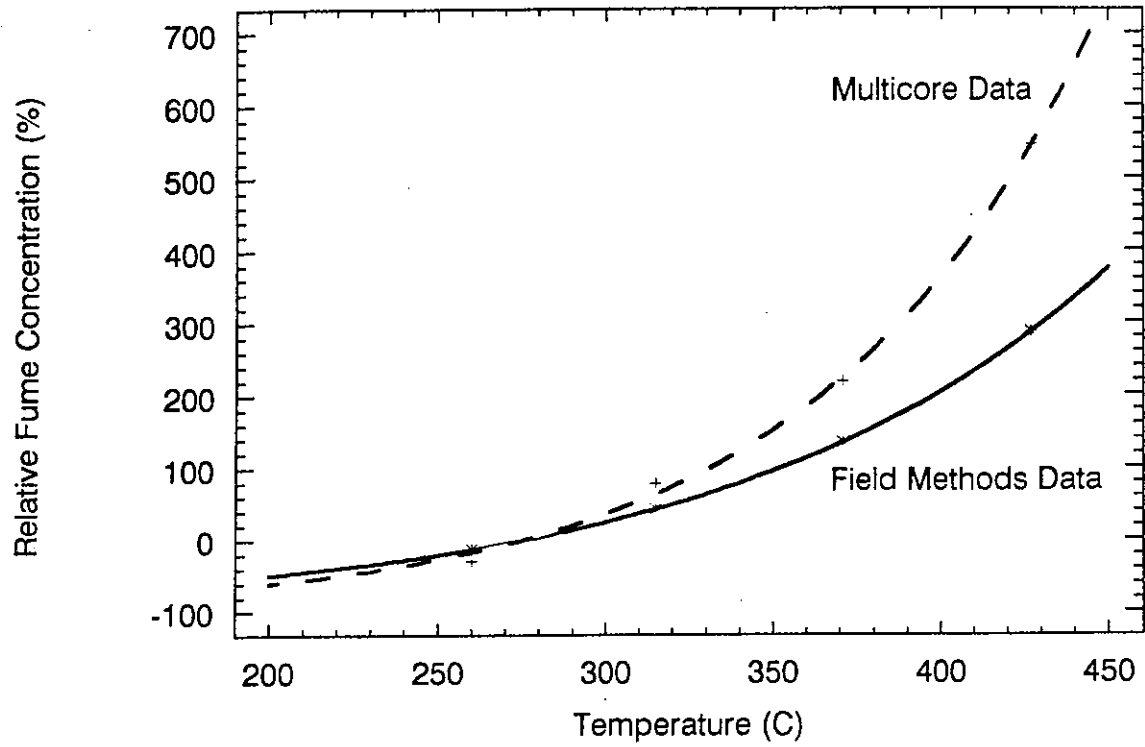
The results of the experiments carried out in this section show that whilst the resin acid composition does not seem to vary significantly within the specified temperature range, the quantity of fume given off by the solder flux increases markedly as temperature rises. Given these results it is clear that significant reductions in fume can be achieved in working environments by reducing soldering iron temperature. It is therefore recommended that where variable temperature soldering irons are provided, the temperature of the soldering iron should be adjusted to the minimum necessary for efficient soldering given the type of solder being used and/or the job being carried out.

5.6 RESIN ACID COMPOSITIONS OF VARIOUS SOLDER TYPES AND GAUGES

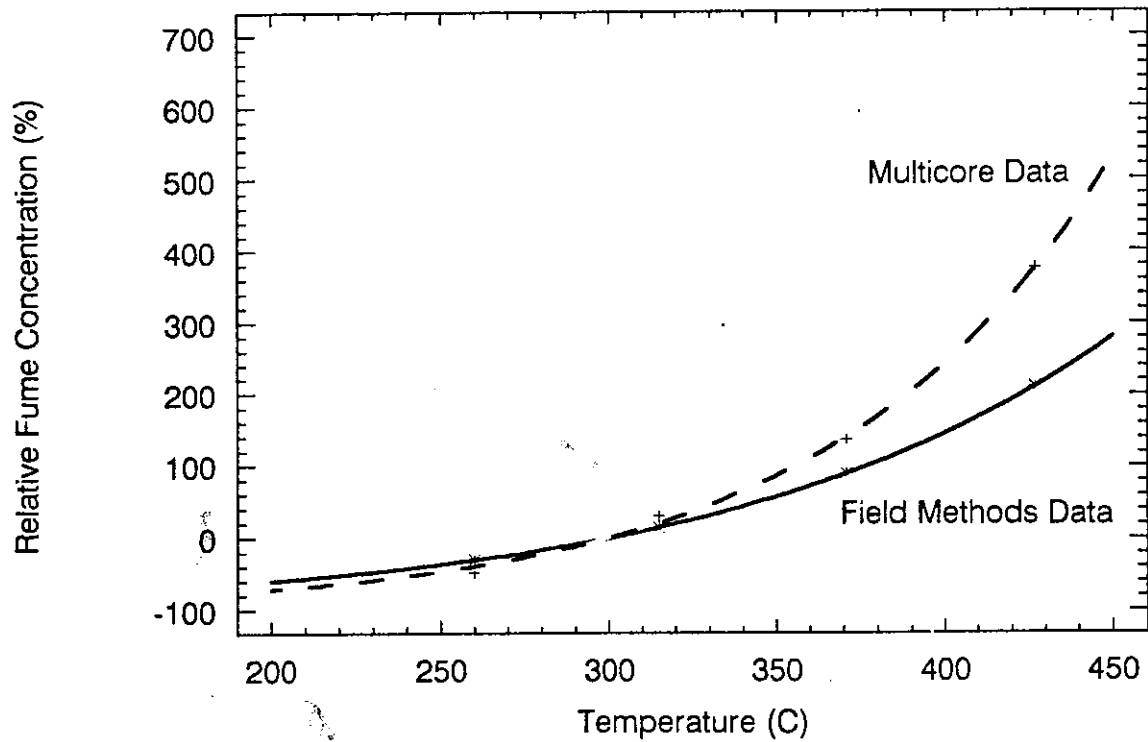
The rosin fluxes from a number of solder types and gauges were extracted into ether and analysed in the usual manner in order to investigate the differences in resin acid composition which occur in a range of solder types and gauges. Altogether the following eleven solder types/gauges were examined.

- A) Savbit 18 SWG 5-Core Solder Wire (This is the solder type used in the majority of the laboratory experiments).
- B) Savbit 1.2 mm 5-Core Solder Wire.
- C) Multicore 18 SWG Ersin 362 Flux Solder Wire.
- D) Multicore 18 SWG 5-Core Ersin Flux Solder Wire.

**FIGURE 7: VARIATION IN SOLDER FUME CONCENTRATION WITH SOLDERING TEMPERATURE.
(RELATIVE TO MINIMUM SOLDERING TEMPERATURE OF 275°C)**



**FIGURE 8: VARIATION IN SOLDER FUME CONCENTRATION WITH SOLDERING TEMPERATURE.
(RELATIVE TO SUGGESTED SOLDERING TEMPERATURE OF 300°C)**



- E) Litesold 18 SWG DTD599 Flux Solder Wire.
 F) Superspeed SN60KP 0.7 mm RS3 Flux Solder Wire (Obtained from a television factory visited).
 G) Multicore 16 SWG Ersin 362 Flux Solder Wire (Obtained from a television factory visited).
 H) Multicore 18 SWG Ersin 362 Flux Solder Wire (Obtained from a television factory visited).
 I) Multicore 22 SWG Ersin 362 Flux Solder Wire (Obtained from a television factory visited).
 J) Multicore 28 SWG Ersin 362 Flux Solder Wire (Obtained from a television factory visited).
 K) Multicore 30 SWG Ersin 362 Flux Solder Wire (Obtained from a television factory visited).

The resin acid compositions of the fluxes contained in the twelve solders above are given in Table 15.

TABLE 15: RESIN ACID COMPOSITION OF TWELVE SOLDER FLUXES

SOLDER TYPE	RESIN ACID TYPE (% OF TOTAL RESIN ACID CONTENT)								
	PIM	SAN	ISO	PAL	RA-5	DHA	ABI	NEO	OTHER
A	8	1	5	8	1	11	55	4	7
B	8	2	5	9	1	7	61	5	2
C	10	2	5	6	2	15	44	5	11
D	9	2	5	6	2	15	44	5	12
E	5	3	18	3	3	17	23	5	23
F	4	3	15	8	1	9	54	4	2
G	7	1	5	9	1	10	57	5	5
H	8	1	4	10	1	9	60	5	2
I	7	1	4	10	1	9	59	5	4
J	7	1	4	10	1	9	59	5	4
K	7	1	4	10	1	10	59	5	3

From the resin acid compositions of the solder fluxes shown in Table 15 the following trends were observed.

The two Savbit solders (A and B) and the five Multicore Ersin solders obtained from the television factory (G to K) were very similar in composition with the only real differences between the seven solders being slight variations in the ABI:DHA ratio. In general the combined abietic-dehydroabietic acid content of these solders was around 66 to 69%, with abietic making up 55 to 61% and dehydroabietic 7 to 11%. The ABI:DHA ratio varied between around 5 and 8:1.

The two Multicore Ersin solders (C and D) showed a slightly lower combined abietic-dehydroabietic content (around 59%) than the seven solders mentioned above. This was mainly due to the markedly lower proportion of abietic acid content of around 45%, resulting in a ABI:DHA ratio of only around 3:1. In addition these two samples showed a number of minor peaks which were almost completely absent from the other Savbit and Multicore solders. These peaks were at around 5 to 5.5 minutes, 9 to 9.5 minutes and 10 to 13.5 minutes. In solders C and D these minor peaks made up some 11 to 12% of the total resin acid content of the sample, whereas in the seven solders above the figure is less than 7%.

The abietic-dehydroabietic acid content of the Litesold solder (E) was around 40% with an ABI:DHA ratio of only around 1.2:1. The main difference between this sample and the Savbit/Multicore fluxes however is the proportion of isopimaric acid present, which at 18% is over three times the percentage present in the Savbit/Multicore solders. At 23%, the minor resin acid peaks also make up a proportion of this sample which is almost twice that of any of the other ten fluxes.

The Superspeed solder (F) had an abietic-dehydroabietic acid content of around 63% with an ABI:DHA ratio of 6:1. As with the Litesold solder, the main difference between this flux and the Savbit/Multicore types is the level of isopimaric acid, which at 15% is around three times higher than these other solders.

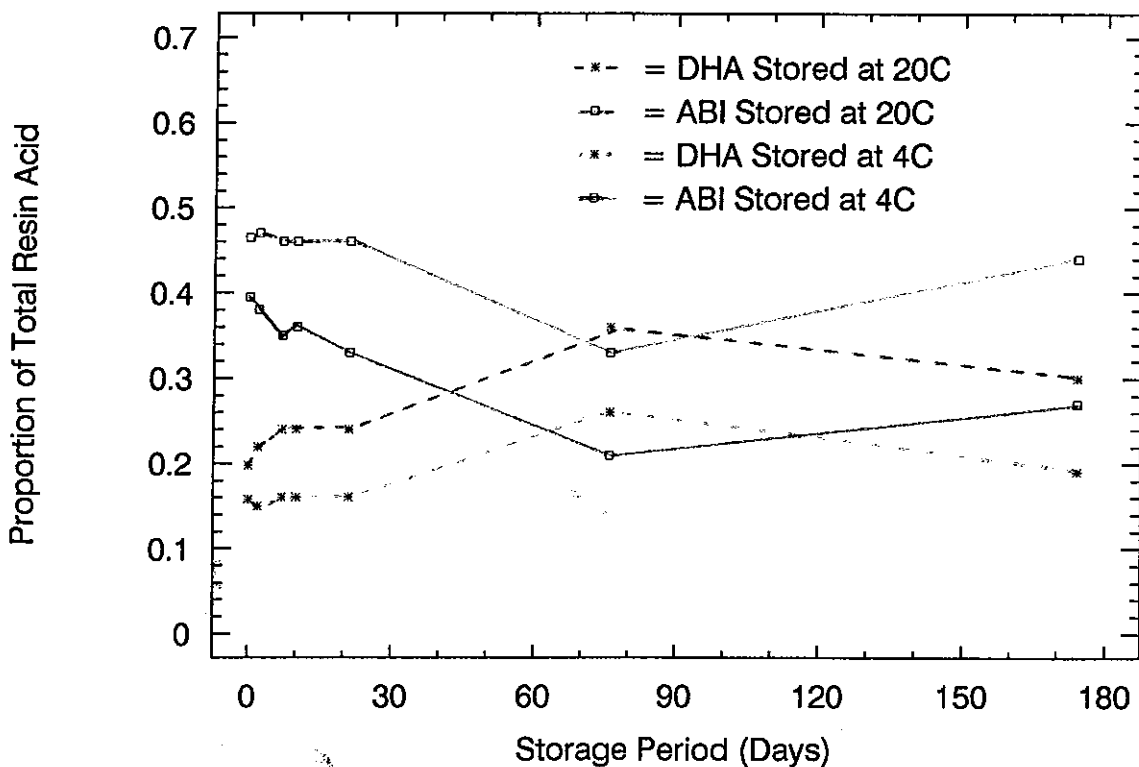
If the levels of the various minor peaks are combined with those for abietic and dehydroabietic acid a slight difference emerges between the Litesold and Superspeed solders (E and F) and the Savbit/Multicore solders tested. In the Litesold/Superspeed solders, this combination of components forms 63 to 65% of the total resin acid content of the flux, whereas for the Savbit/Multicore solders this figure is 70 - 73%. The relatively constant nature of this figure for the Savbit/Multicore solders suggests that as all the solders are likely to have started out with a similar composition, the variations in dehydroabietic acid and many of the various minor peaks probably result from the decomposition of abietic acid. Solders E and F however would appear to have had a slightly different initial composition in which the abietic-dehydroabietic acid content is slightly lower, although in both cases this is largely compensated for by an increase in the proportion of isopimaric acid present (the two solders vary slightly in the amounts of pimaric and palustric acid present).

5.7 SAMPLE STORAGE

This experiment was intended to determine the stability of resin acid samples collected onto filters and stored for varying periods of time prior to analysis. From the results of previous experiments it was expected that the proportion of abietic acid in particular would be shown to decrease with time, and given this it was hoped to determine a recommended maximum storage period for the filters. Exposed sample filters were stored in sealed brass tins at both room temperature and in the fridge to see if storage temperature affected sample stability.

Two sets of six 13 mm Millipore-MF filters were loaded into standard filter holders and used to sample solder fume atmospheres over a 10 minute sampling period at 1 l/min in the standard atmosphere chamber. Both atmospheres were generated from approximately 12 cm of 18 SWG 5-Core Multicore solder wire.

FIGURE 9: EFFECT ON ABIETIC AND DEHYDROABIETIC CONTENT OF FILTER STORAGE



After sampling, the filters were placed in brass tins and cut in half with a scalpel blade. One half of each filter was removed for GC analysis in the usual manner, and the other re-sealed in the brass tin and stored for between 2 and 174 days analysis (see Table 16). Filters 1 to 6 were stored at room temperature (*ca.* 20°C) and Filters 7 to 12 re-refrigerated (*ca.* 4°C).

The results of the various analyses are detailed in Table 16 and shown graphically in Figure 9. The main observations are that when stored at room temperature, changes in the resin acid ratios (abietic and palustric decreasing, pimaric and dehydroabietic increasing) begin to occur on the filter after only 2 to 7 days. However, when stored in a fridge at a temperature of around 4°C, the samples show no significant changes in composition after several weeks. Indeed, Filter 12 showed relatively little change in resin acid composition between the half analysed immediately and the half stored under refrigeration for almost 6 months.

TABLE 16: EFFECT OF STORING FILTERS PRIOR TO ANALYSIS

FILTER NUMBER	STORAGE (days)	STORAGE (°C)	PIM (%)	SAN (%)	ISO (%)	PAL (%)	RA-5 (%)	DHA (%)	ABI (%)	NEO (%)	TRA
1	0	---	11	2	6	13	4	19	40	5	272
	2	20	11	2	6	12	4	22	38	5	275
2	0	---	11	2	6	13	4	20	40	4	196
	7	20	12	3	6	11	5	24	35	4	258
3	0	---	11	2	6	13	4	20	40	4	206
	10	20	11	2	6	11	5	24	36	5	343
4	0	---	11	2	6	13	4	19	40	5	247
	21	20	12	3	6	11	6	24	33	5	244
5	0	---	11	2	6	13	4	20	39	5	256
	76	20	15	2	7	6	8	36	21	5	156
6	0	---	11	2	6	13	4	21	38	5	303
	174	20	13	3	7	9	7	30	27	4	198
7	0	---	10	2	5	15	1	15	47	5	311
	2	4	10	2	5	15	1	15	47	5	378
8	0	---	10	2	5	14	2	16	46	5	254
	7	4	10	2	5	14	2	16	46	5	279
9	0	---	10	2	5	14	2	16	46	5	256
	10	4	10	2	5	14	2	16	46	5	348
10	0	---	10	2	5	14	2	15	47	5	228
	21	4	10	2	5	14	2	16	46	5	286
11	0	---	10	2	5	14	1	16	47	5	400
	76	4	13	2	7	11	3	26	33	5	219
12	0	---	10	2	5	14	2	17	46	4	266
	174	4	11	2	6	14	2	19	44	2	273

From these experiments the recommended maximum filter storage times are as follows.

- a) For sample sealed in brass tins at room temperature - 1 week
- b) For samples sealed in brass tins below at 4°C - 6 months

5.8 SUMMARY OF RESULTS

The experiments in Section 5 have produced the following results and observations.

Solder flux obtained from solvent extraction of solder at room temperature has a combined abietic-dehydroabietic acid content of around 70%, whereas for solder fume generated at a soldering iron tip at around 300°C this figure is reduced to around 60%. It is thought that this difference may be due to heat induced isomerisation of abietic acid^(22,23).

Increasing soldering iron temperature between 210 and 405°C produces no significant changes in the resin acid composition of the evolved fume, however it does lead to an exponential increase in the quantity of fume produced from a given length of solder. Soldering iron temperature should therefore be kept to the minimum necessary for the soldering application in order to reduce the quantity of fume released into the local atmosphere.

Drawing clean air through a filter loaded with solder fume causes the proportion of abietic acid to decrease slightly and the proportion of dehydroabietic to increase slightly. The result of this is that the sum of the two components stays more or less the same, suggesting that at room temperature abietic acid decomposes into dehydroabietic acid (rather than isomerising to produce quantities of palustric and neoabietic as is thought to happen above 200°C). This observation appears to be independent of both filter type (Millipore-MF, DM800, PTFE or Whatman#3) and size (13 or 25 mm). The small changes in the absolute proportions of abietic and dehydroabietic acid with increased sampling time does however lead to quite significant decreases in the ABI:DHA ratio.

Varying the total resin acid concentration in the sample between 0 and 800 µg/ml produces no significant affect on the the resin acid composition of samples. This suggests that evaporation of solvent from the samples during the work-up procedure does not cause any additional reaction/oxidation of the abietic acid fraction of the sample.

Different types of solder flux have different resin acid compositions. Of the types tested, the Savbit and Multicore fluxes all have fairly similar compositions, which differs from that in Litesold and Superspeed fluxes. The Litesold and Superspeed solders contain fluxes which show certain similarities in composition, but which also have significant differences.

Storage experiments have shown that when sealed in small brass tins the sample filters are stable for around 1 week at room temperature and up to six months if kept at 4°C.

Overall, the main conclusion of these experiments is that once on the filter, the proportion of abietic and dehydroabietic acid combined remains fairly constant, although the individual proportions of the two resin acids may show some change on exposure to air.

6. PERSONAL SAMPLING METHOD FOR RESIN ACIDS IN SOLDER FUME

6.1 PROPOSED SAMPLING METHOD

The proposed sampling method was to collect both particulate and volatile fractions of the solder fume by using a combination of membrane filter and charcoal tube. The filter used is a 13 mm Millipore-MF type contained in a standard Millipore Swinnex 13 mm filter holder connect. to a standard SKC charcoal adsorbent tube.

The particulate samples will be solvent extracted from the filter before methylation and gas chromatographic analysis as described in Section 3. The volatile samples will be desorbed in carbon disulphide and also be analysed by GC as described in Section 2.

It is proposed that samplers be located on both the lapel and in the breathing zone for comparison (see Section 6.4).

The following paragraphs detail the development of the proposed sampling method.

6.2 FILTER PORE SIZE AND SAMPLING EFFICIENCY

The proposed sampling system employs a 13 mm RAWP Millipore MF filter which has a 1.2 μm pore size. At the proposed sampling rate of 1 l/min this generates significant back-pressure, particularly when used in combination with a standard charcoal tube. In the laboratory this is not particularly significant since air sampling can be carried out using a mains driven sampling pump, however for personal sampling, such a pump is not acceptable and must be replaced by a battery driven portable sampling pump. Portable sampling pumps are much more limited in their performance and endurance than a mains driven pump, and typically, have a back-pressure limit of around 35 to 40" of water if the pump, when fully charged, is to run for a full 8 hour sample.

To illustrate this point, five Millipore filter heads were loaded with 13 mm RAWP filters and connected to a standard SKC charcoal tube and an SKC portable sampling pump. One pump was set to run at 500 ml/min, two at 750 ml/min and the final two at 1000 ml/min. The filter heads were then placed in the atmosphere chamber and left to sample fume generated from around 12 cm of 18 SWG Savbit solder heated to 321°C over a period of around 10 minutes. Once loaded with fume the filters were left sampling "clean" air for until their respective pumps stopped running. The results were as follows.

- Pump 1 (500 ml/min) = 399 minutes (6 hrs 39 minutes).
- Pump 2 (750 ml/min) = 116 minutes (1 hr 56 minutes).
- Pump 3 (750 ml/min) = 505 minutes (8 hrs 25 minutes).
- Pump 4 (1000 ml/min) = 372 minutes (6 hrs 12 minutes).
- Pump 5 (1000 ml/min) = 553 minutes (9 hrs 13 minutes).

From these results it would appear that in a fully charged state the pumps are probably capable of pulling 1 l/min through a 13 mm RAWP filter and charcoal tubes for six hours, but probably not eight (the reason for Pump 2 stopping is unclear). It should also be noted that the filters in this case were only moderately loaded with fume, although if heavier loadings were anticipated, the system could be run at a lower flow rate since the GC analysis has sensitivity in reserve at these levels.

The results given in Table 17 indicate that at a sampling rate of 1 l/min the back-pressure from an 1.2 μm RAWP filter alone is around 28" of water, rising to over 50 when used in combination with a standard charcoal tube. This is clearly not acceptable for 8-hour sampling with a battery driven portable sampling pump. If RAWP filters were to be used in personal sampling devices then either lower flow rates or shorter sampling times would have to be employed (which would in turn decrease the detection limit). An alternative however is to use a larger pore size filter as this would reduce the back-pressure, whilst retaining the sampling characteristics of the RAWP filter. Examples of Millipore MF filters of 3.0 and 5.0 μm pore size (known as SSWP and SMWP respectively) were obtained, and back-pressure measurements taken to see if they offered any significant improvement in this respect.

The results of these measurements are given in Table 17, and show a large difference between the 1 and 3 μm filters, with a much smaller difference between the 3 and 5 μm filters. When used in combination with a standard charcoal tube the back-pressure measurements indicate that both the SSWP and SMWP filters could be used over a full 8-hour

sampling period with a fully charged portable sampling pump. The SSWP however is close to the borderline of acceptability, particularly as in these tests the filters used are clean, and that as the concentration of dust particles on the filter increases, so will the back-pressure.

TABLE 17: BACK-PRESSURE MEASUREMENTS OF VARIOUS FILTERS & SAMPLING DEVICES.

SAMPLING DEVICE	BACK-PRESSURE (inches water)
13 mm SMWP Filter (5 µm Pore Size)	10
13 mm SSWP Filter (3 µm Pore Size)	13
13 mm RAWP Filter (1.2 µm Pore Size)	28
Charcoal Tube 1	22
Charcoal Tube 2	22
Charcoal Tube 3	18.5
Charcoal Tube 4	24
Charcoal Tube 5	20
Charcoal Tube (Mean)	21.3
SMWP Filter + Charcoal Tube 5	34
SSWP Filter + Charcoal Tube 5	38
RAWP Filter + Charcoal Tube 5	ca. 50 (est.)

Although the change to a larger pore size filter has decreased the back-pressure however, it is important that it has not done so at the expense of sampling efficiency. The following set of experiments was therefore carried out to compare the sampling efficiency of the three filter types.

Twenty filters, consisting of eight RAWP, six SSWP and six SMWP, were loaded into standard 13 mm Millipore filter heads. Each filter head was then connected in series to a filter head containing a filter of the same type to give ten sets of double filters. Air containing solder fume generated at around 300°C from a soldering iron tip was then drawn at 1 l/min through the pairs of filters, which were then analysed for total resin acid (TRA) content in the usual way. The sampling efficiency of the front filter from each pair was calculated as a percentage of the total resin acid collected on both the front and back filter. The results from all ten pairs of filters are given in Table 18.

TABLE 18: SAMPLING EFFICIENCY OF MF-MILLIPORE FILTERS.

FILTER NUMBER	FILTER TYPE	PORE SIZE (µm)	TRA ON FILTER (µg)			SAMPLING EFFICIENCY (%)
			FRONT	BACK	TOTAL	
1	RAWP	1.2	430	13.0	444	97.0
2	RAWP	1.2	272	3.0	275	98.9
3	RAWP	1.2	375	4.0	379	98.9
4	RAWP	1.2	500	4.0	504	99.2
Mean	---	---	---	---	---	98.5
5	SSWP	3.0	213	1.2	214	99.4
6	SSWP	3.0	205	1.3	207	99.4
7	SSWP	3.0	165	1.2	166	99.2
Mean	---	---	---	---	---	99.3
8	SMWP	5.0	194	1.3	196	99.3
9	SMWP	5.0	227	1.6	229	99.3
10	SMWP	5.0	178	3.1	181	98.3
Mean	---	---	---	---	---	99.0

The results in Table 18 appear to show no significant difference in sampling efficiency for the three pore sizes of Millipore-MF filter tested, with all three being virtually 100% (within experimental error). Any one of these three pore size filters can therefore be used with equal sampling efficiency, and, since the 5.0 μm SMWP has the lowest back-pressure of the three, this type has been adopted for sampling solder fume.

6.3 FILTER HEAD EXPERIMENT

This experiment was designed to determine if there were any losses of solder fume due to electrostatic attraction onto the internal walls of the standard 13 mm Millipore Swinnex filter head.

Five SSWP filters were loaded into standard 13 mm filter heads. Two of the filter/holder combinations were put to one side for use as blanks, whilst the other three were placed in a glass chamber and used to sample fume generated from approximately 12 cm of 18 SWG solder heated to around 300°C. The filters sampled at the standard rate of 1 l/min and the total sampling period was around 10 minutes. After sampling, the three sample filters and the two blanks were removed for analysis of resin acids by the usual procedure. The plastic top sections from the five samplers were placed in 10 ml glass beakers and rinsed with 5 ml of ether. The ether washings from each filter head were then evaporated to dryness and also analysed for resin acid content. The results are shown in Tables 19 and 20.

The figures in Table 19 show minor GC peaks in the resin acid region to be present on both the unexposed filters and plastic head material. There is also a more much more noticeable peak in the region of dehydroabiatic acid on the traces obtained from both unexposed plastic head samples. The effects of all these "blank" peaks can be removed from the three exposed samples to obtain the figures given in Table 20.

The Total Resin Acid (TRA) column in Table 20 indicates that the relative amounts collected on filter and plastic head for the three samplers exposed to solder fume were 98.80 and 1.20% for Sampler 3, 98.84 and 1.16% for Sampler 4 and 98.90 and 1.10% for Sampler 5. This gives an average for the three samplers of 98.85% of the collected sample on the filter and 1.15% on the plastic head material. These results suggest that the amount of sample which is attracted onto the filter head material is fairly insignificant and can therefore be safely ignored.

TABLE 19: RESIN ACID CONTENT OF SOLDER FUME PARTICLES RECOVERED FROM SAMPLE FILTERS AND PLASTIC FILTER HOLDERS

SAMPLE	PIM	SAN	ISO	PAL	RA-5	DHA	ABI	NEO	OTH	TRA
Filter 1 (Blank)	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Head 1	0.0	0.0	0.0	0.2	0.0	7.6	0.3	0.2	0.7	9.0
Filter 2 (Blank)	0.0	0.1	0.0	0.1	0.0	0.0	0.3	0.0	0.1	0.5
Head 2	0.0	0.0	0.0	0.2	0.0	7.9	0.0	0.8	3.8	12.8
Filter 3 (Sample)	83.0	14.4	48.2	156.5	19.4	174.9	412.3	51.8	67.1	1027.6
Head 3	1.0	0.1	0.7	1.9	0.0	11.1	5.6	0.8	2.1	23.2
Filter 4 (Sample)	95.3	16.8	53.8	176.0	22.4	190.9	468.2	57.6	77.2	1158.2
Head 4	1.1	0.0	0.7	2.0	0.0	12.0	5.1	1.2	2.3	24.5
Filter 5 (Sample)	95.8	16.4	55.8	177.8	23.9	197.7	474.3	59.0	73.8	1174.5
Head 5	1.0	0.1	0.7	1.8	0.0	11.3	4.8	0.8	3.5	23.9

TABLE 20: BLANK CORRECTED RESIN ACID COLLECTION DATA

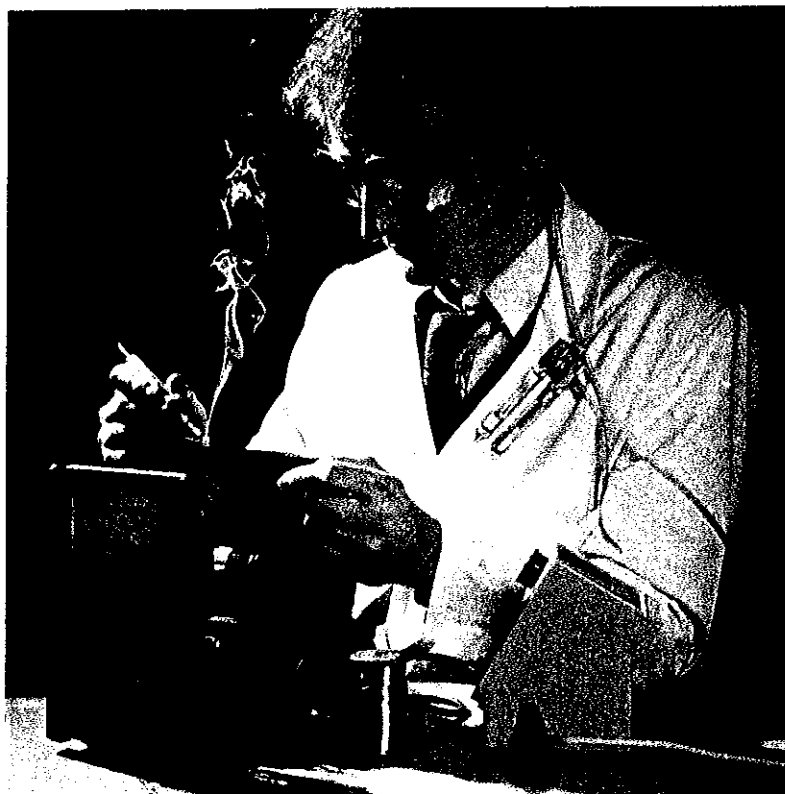
SAMPLE	PIM	SAN	ISO	PAL	RA-5	DHA	ABI	NEO	OTH	TRA
Filter 3	83.0	14.3	48.2	156.4	19.4	174.9	412.2	51.8	67.1	1027.3
Head 3	1.0	0.1	0.7	1.7	0.0	3.4	5.4	0.3	0.0	12.5
Filter 4	95.2	16.7	53.8	175.9	22.4	190.9	468.1	57.6	77.2	1157.9
Head 4	1.1	0.0	0.7	1.8	0.0	4.2	4.9	0.7	0.1	13.6
Filter 5	95.8	16.3	55.8	177.8	23.9	197.7	474.2	59.0	73.7	1174.2
Head 5	1.0	0.1	0.7	1.6	0.0	3.6	4.6	0.3	1.2	11.8

6.4 BREATHING ZONE VERSUS LAPEL SAMPLING

It had been noticed on previous sampling visits⁽⁶⁾, and in our own laboratory experiments, that solder fume tends to rise in a plume from the solder iron tip rather than spread out uniformly into the surrounding area. Often this means the fume is rising into the breathing zone, and so the traditional lapel sampling region may be considerably underestimating the airborne fume concentration to which a solderer is exposed. To overcome this, a breathing zone sampler was constructed consisting of standard 13 mm sampling heads attached to modified pairs of plastic safety spectacles (see Figure 10).

The results of the lapel versus breathing zone sampling comparisons are given in Section 7 dealing with field trials.

FIGURE 10: OPERATOR WEARING SOLDER FUME SAMPLING DEVICE IN LAPEL AND BREATHING ZONE POSITIONS



6.5 SAMPLING RATES

6.5.1 Low Flow Rate Samples

Low flow rate samples can be taken using a battery powered portable sampling pump to draw air through a 13 mm Millipore-MF filter (pore size 5.0 microns) connected to a standard SKC charcoal tube. The maximum flow rate which can be achieved with this sampling system is around 1.2 l/min, however this is with a clean filter. For "real-life" samples a maximum flow rate of 1 l/min is recommended because the back-pressure of the sampling system tends to rise as dust and fume is deposited onto the filter. Fully charged pumps have been found to be capable of drawing air through such a fume laden samplers at 1 l/min for periods in excess of 6 hours.

If the charcoal tube is removed from the sampling system, the maximum flow rate can be increased to around 2.2 l/min, although for "real-life" samples a maximum of rate of 2 l/min is recommended. Fully charged pumps have been found to be capable of drawing air through this type of sampler at 2 l/min for periods in excess of 8 hours, however this higher flow rate is really only necessary to achieve higher sensitivity in short term 10 and 15 minute samples.

6.5.2 High Flow Rate Samples

As solder fume is considered to be a respiratory sensitiser, there is a requirement to be able to measure exposures over very short time periods. This can be achieved by the use of high flow rate (*ca.* 50 l/min) samplers, using a Rotheroe & Mitchell L60 main driven sampling pump and 37 mm Millipore-MF or DM800 filter. The same type of sampler can also used to obtain long-term static background samples.

The short-term personal samples use the pumps with the 37 mm sampling head positioned remotely and attached to the pump via a length of reinforced plastic tubing. During sampling, the sampling head is either fixed or held manually in the vicinity of the solderer, ideally positioned as close to the breathing zone of the solderer as possible. Typically these samples are of 5 - 15 minutes duration giving a sample volume of 0.25 - 0.75 m³.

The long-term background samples use the pumps with the sampling head mounted directly onto the pump. The samplers are simply left standing on a convenient surface in the work area for the duration of the sampling period. Typically samples are of 1 - 6 hours duration giving a sample volume of 3 - 18 m³. Care must be taken with these long term samples to ensure that the sampling rate does not fall below the minimum reading of 40 l/min (ideally the sample should be stopped and a fresh one started when the sampling rate reaches 42 l/min).

6.6 ESTIMATION OF DETECTION LIMITS

The resin acid calibration samples on the GC have shown that a minimum total resin acids (TRA) peak area of around 250 units is required in order to obtain measurable resin acid peaks. Using the FID response factor of 73.38 calculated in Section 5.4.4, this is equivalent to around 3.4 ng of resin acid, which represents a concentration in the sample solution of 3.4 µg/ml for a 1 µl injection and 1.7 µg/ml for a 2 µl injection.

Each sample solution consists of the resin acid sample collected on the sample filter dissolved into a minimum of 0.3 ml of toluene/N,N-dimethyl formamide dimethyl acetal. Thus, the minimum resin acid content of the sample solution is around 1.02 µg for a 1 µl injection and 0.51 µg for a 2 µl injection.

Ideally a total resin acid peak area of around 3000 is required. This is equivalent to around 41 ng of resin acid, and represents a concentration in the sample solution of around 41 and 20 µg/ml for 1 and 2 µl injections respectively. These figures represent a resin acid content in the sample solution of around 12.3 µg for a 1 µl injection or 6.1 µg for a 2 µl injection.

From these figures the minimum sample volumes shown in Table 21 for a range of airborne total resin acid concentrations can be calculated.

TABLE 21: MINIMUM SAMPLE AIR VOLUMES FOR AIRBORNE TOTAL RESIN ACID

TRA ($\mu\text{g}/\text{m}^3$)	1 μl INJECTION		2 μl INJECTION	
	SV1	SV2	SV1	SV2
1	1022	12265	511	6132
5	204	2453	102	1227
10	102	1227	51	613
25	41	491	21	245
50	21	245	10	123
75	14	164	7	82
100	10	123	5	61
150	7	82	4	41
200	5	61	3	31
500	2	25	1	12

SV1 = Sample Volume in litres required to give a Peak Area of 250.
 SV2 = Sample Volume in litres required to give a Peak Area of 3000.

Once these minimum sample volumes have been determined, the minimum sampling times necessary at various sampling rates can be calculated. These are shown in Tables 22 and 23 for sampling rates of 1 and 2 l/min (personal samplers) and 50 l/min (L60 samplers). From these minimum sampling rates, the detection limits shown in Table 24 for 10 minute and 6 hour (360 minute) samples at the three sampling rates can be calculated.

Table 24 indicates that sampling over 10 minutes at 2 l/min, and using a 2 μl injection into the GC, the detection limit is around 25 - 30 $\mu\text{g}/\text{m}^3$. By reducing the volume of the final solution in the work-up procedure to 150 μl , it should be possible to reduce this detection limit to around 12 - 15 $\mu\text{g}/\text{m}^3$.

TABLE 22: MINIMUM SAMPLING TIMES FOR AIRBORNE TRA AT 1 AND 2 l/min.

TRA ($\mu\text{g}/\text{m}^3$)	SAMPLING AT 1 l/min				SAMPLING AT 2 l/min			
	1 μl INJECTION		2 μl INJECTION		1 μl INJECTION		2 μl INJECTION	
	ST1	ST2	ST1	ST2	ST1	ST2	ST1	ST2
1	1022	12265	511	6132	511	6132	256	3066
5	204	2453	102	1227	102	1227	51	613
10	102	1227	51	613	51	613	26	307
25	41	491	21	245	21	245	10	123
50	21	245	10	123	10	123	5	61
75	14	164	7	82	7	82	3	41
100	10	123	5	61	5	61	3	31
150	7	82	4	41	4	41	2	20
200	5	61	3	31	3	31	1	15
500	2	25	1	12	1	12	1	6

ST1 = Sampling Time in minutes required to give a Peak Area of 250.
 ST2 = Sampling Time in minutes required to give a Peak Area of 3000.

TABLE 23: MINIMUM SAMPLING TIMES FOR AIRBORNE TRA AT 50 l/min.

TRA ($\mu\text{g}/\text{m}^3$)	1 μl INJECTION		2 μl INJECTION	
	ST1	ST2	ST1	ST2
1	20.44	245.30	10.22	122.65
5	4.09	49.06	2.04	24.53
10	2.05	24.53	1.02	12.26
25	0.82	9.81	0.41	4.91
50	0.41	4.91	0.20	2.45
75	0.27	3.27	0.14	1.64
100	0.20	2.45	0.10	1.23
150	0.14	1.64	0.07	0.82
200	0.10	1.23	0.05	0.61
500	0.04	0.49	0.02	0.25

ST1 = Sampling Time in minutes required to give a Peak Area of 250.
 ST2 = Sampling Time in minutes required to give a Peak Area of 3000.

TABLE 24: TOTAL RESIN ACID DETECTION LIMITS AT 1, 2 AND 50 l/min

SAMPLING RATE (l/min)	SAMPLING TIME (mins)	1 μl INJECTION		2 μl INJECTION	
		DL1	DL2	DL1	DL2
1	10	102	1230	51.1	613
2	10	51.1	615	25.6	308
50	10	2.04	24.5	1.02	12.3
1	360	2.84	34.1	1.42	17.0
2	360	1.42	17.1	0.71	8.5
50	360	0.06	0.68	0.03	0.34

DL1 = Detection Limit in $\mu\text{g}/\text{m}^3$ for a Peak Area of 250.
 DL2 = Detection Limit in $\mu\text{g}/\text{m}^3$ for a Peak Area of 3000.

6.7 SOLDER FUME PARTICLE SIZE

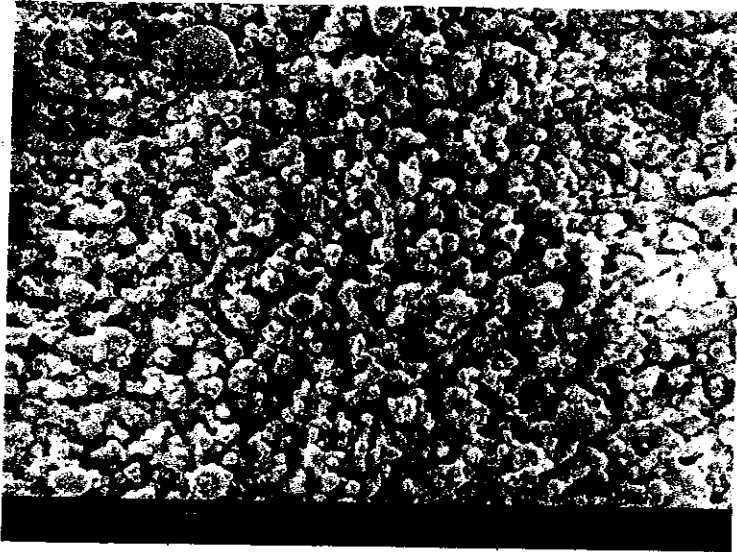
An experiment was carried to examine the typical particle size range of solder fume sampled onto a membrane filter using a scanning electron microscope. The main purpose of this experiment was to determine whether significant levels of agglomeration of solder fume particles was occurring during sampling, as it is possible that such agglomeration might affect the sampling characteristics of the filter.

Using the standard atmosphere chamber, a sample of solder fume generated from Savbit solder heated to around 300°C, was deposited onto a nucleopore filter (1 micron pore size). The sample was taken using around 10 cm of 18 SWG solder over a 10 minute sampling period at around 1 l/min.

The filters were passed to the Dust Investigation Section for examination with a scanning electron microscope. Figure 13 shows three views of the solder fume particulate collected onto the surface of the filter at different magnifications. The pictures indicate a particle size range for the particulate of around 0.5 - 5 microns, although some particles have agglomerated into small clusters or chains of up to 20 microns in length.

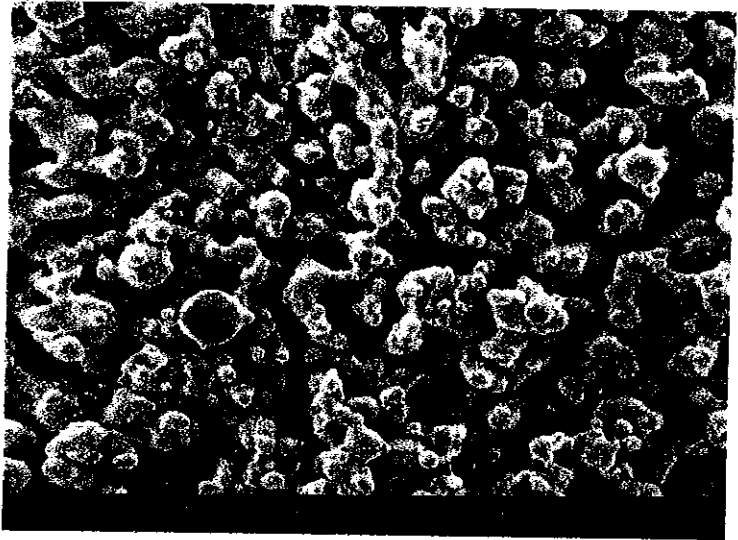
Such low levels of particulate agglomeration, even in a quite heavily loaded filter, lead to the conclusion that it is unlikely that the sampling characteristics of the filter will change significantly whilst sampling solder fume.

FIGURE 11: SEM PHOTOGRAPHS OF SOLDER FUME PARTICULATE



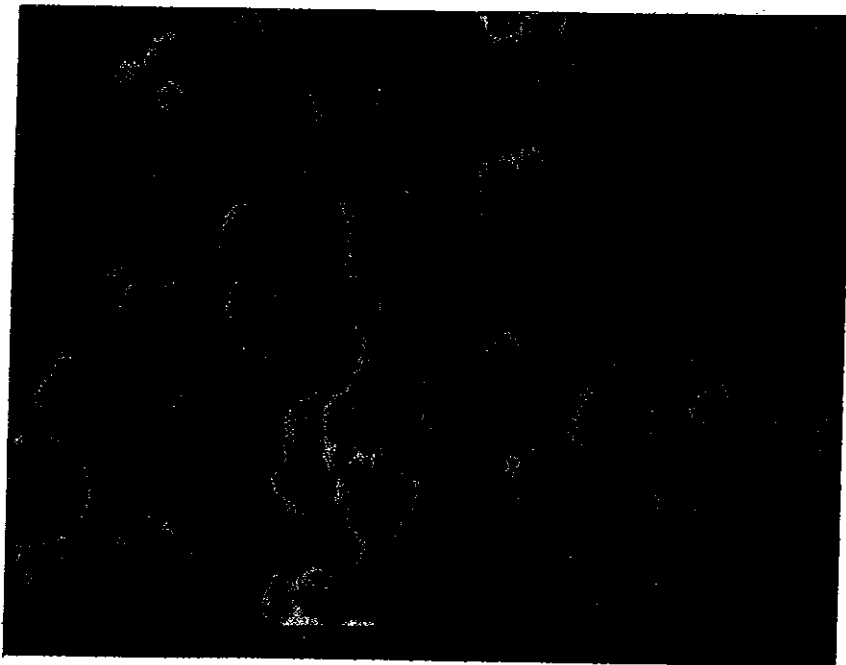
PHOTOGRAPH A

Field of View = 100 x 70 microns



PHOTOGRAPH B

Field of View = 50 x 35 microns



PHOTOGRAPH C

Field of View = 23 x 17 microns

7. FIELD TRIALS

The sampling method was evaluated in a series of field trials on the premises of three companies whose work involved the soldering of electrical and/or electronic components.

7.1 SAMPLING METHODS

7.1.1 Sample Types

At each location a mixture of low and high flow rate personal samples and high flow rate background samples were taken.

The low flow rate personal samples were taken in pairs with one sampler being located on the lapel of the person being sampled, and the other in his/her breathing zone (attached to a modified pair of safety spectacles). Each personal sampler consisted of a 13 mm Millipore-MF filter in a standard cassette filter holder connected in series to an SKC charcoal tube to collect the particulate and volatile fractions of the fume respectively. The personal samplers were attached to portable sampling pumps worn around the waist of the solderer. Sampling rates were approximately 1 l/min, with sampling periods of between 1 and 6 hours.

The high flow rate personal samples were taken onto 37 mm Millipore-MF or DM800 filters loaded into a metal sampling head attached to an L60 mains sampling pump with reinforced plastic tubing. The sampling head was held in the breathing zone of the solderer for a period of approximately 10 minutes at a sampling rate of around 50 l/min.

The background samplers consisted of 37 mm Millipore-MF or DM800 filters loaded in metal sampling heads attached to L60 mains samplers running at around 50 l/min for time periods varying from 1 to 6 hours.

After sampling, the high flow rate sample filters (both personal and background) were removed from the filter heads and placed in brass tins for transport. The 13 mm filters were left in the sampling heads which were placed in sealed plastic bags. All samples were analysed within 48 hours of sampling, with overnight storage, where necessary, in a fridge at approximately 4°C.

A total of 52 samples were taken on three visits consisting of 18 low flow rate personal samples (9 pairs of lapel/breathing zone samples), 19 high flow rate personal samples and 15 high flow rate background samples. The sample type can be identified by the following code in the sample number.

- a) **LPL** - Low flow rate Personal sampler located on the Lapel.
- b) **LPB** - Low flow rate Personal sampler located in the Breathing zone.
- c) **HPB** - High flow rate (L60) Personal sampler located in the Breathing zone.
- d) **HBG** - High flow rate (L60) Background sampler.

Sample volumes were calculated by measuring flow rates before and after sampling to give the mean flow rate which was then multiplied by the sampling time.

7.1.2 Analysis of Filter Samples

Each sample was desorbed from the filter into ether (5 ml + 2 ml rinse), before being evaporated to dryness and methylated with a solution of DMF-acetal in toluene (0.2 ml) at 60°C. At this point an internal standard of methyl stearate in toluene (0.2 ml) was added. The concentration of the internal standard was 949 µg/ml so the methyl stearate content of each sample was 189.8 µg. 1 µl injections of each sample were made onto the GC and the resin acid content for each calculated from their peak areas relative to methyl stearate (474.5 ng).

In addition the L60 samples were weighed before and after sampling for gravimetric analysis for total dust sampled before desorption for comparison with the GC results.

7.1.3 Analysis of Charcoal Tube Samples

The personal samplers incorporated charcoal tubes for the measurement of any airborne volatile substances present. After sampling, the charcoal was solvent desorbed with 500 µl of carbon disulphide containing a small amount of an internal standard of dodecane. After standing for approximately 30 minutes, the sample solutions were then analysed by GC.

7.1.4 Sample Blanks

Sample blanks for each of the three sample filter types and for the charcoal tubes were also analysed using the same procedure outlined above for the actual samples.

7.2 FIELD TRIAL AT A TELEVISION REPAIR FACILITY (I)

The first field trial was carried out on the premises of a company repairing televisions, videos and other domestic audio-visual equipment on July 29th 1992. The process involved finding the faults in printed circuit boards (PCBs) followed, where necessary, by the removal and replacement of electronic components from those boards. Soldering operations were fairly limited on the day of the visit, with only one operator carrying out limited soldering and desoldering operations. Sampling was therefore discontinued after a time period of 85 minutes, of which some 15 - 20 minutes was spent in soldering/desoldering operations (around 50% on each). Of the two operations it was noticeable that the soldering of new components onto the PCB generated visibly more fume than the desoldering and removal of the old components.

A total of 7 solder fume samples were taken onto Millipore MF cellulose acetate-nitrate membrane filters. These consisted of 2 low flow rate personal samples (1 pair of lapel/breathing zone samples), 2 high flow rate personal samples and 3 high flow rate background samples. The locations of the various samplers were are given in Table 25.

TABLE 25: SAMPLING DETAILS FROM FIELD TRIAL 1

SAMPLE NUMBER	SAMPLING LOCATION	SAMPLING RATE (l/min)	SAMPLING TIME (mins)	SAMPLE VOLUME (m ³)
LPL01	Personal Sample (Lapel)	1.00	85	0.0850
LPB02	Personal Sample (B-Zone)	0.97	85	0.0829
HPB03	Personal Sample (B-Zone)	52.50	3	0.1575
HPB04	Personal Sample (B-Zone)	53.50	5	0.2675
HBG05	Background (ca. 2 ft from Soldering)	48.50	99	4.8015
HBG06	Background (ca. 10 ft from Soldering)	48.11	92	4.4260
HBG07	Background (Outside in Car Park)	46.94	93	4.3650

7.2.1 Filter Samples

The sample chromatograms showed a number of components with similar retention times to the resin acids, including some which caused significant interference, particularly for those samples with very low resin acid concentrations. For this reason, the sample collected from the car park was used as a sampling blank. The airborne concentrations of the 10 main resin acids were calculated from the relative peak areas in all seven samples, and from these values were then subtracted those obtained from the sample collected in the car park.

Table 26 shows the amount of total resin acid in a 1 µl injection of each of the seven sample solutions calculated from the relative peak areas obtained in the GC analysis. The table also gives the airborne total resin acid concentration obtained from these concentration after being blank corrected with sample HBG07 obtained from the car park.

The results show the two background L60 samples (HBG05 and HBG06) giving airborne total resin acid concentrations of well under 1 µg/m³. Sample HBG06 which was located about 10 feet from the soldering operation gave an airborne concentration of effectively zero, whilst Sample HBG05 which was only some 2-3 feet from the soldering operation gave 0.41 µg/m³. These samples would appear to show that general background levels of resin acids are very low, even quite close to the source of the fume.

The results of the two high volume samples taken in the breathing zone of the operative were much higher. Sample HPB03 was collected whilst the operator was carrying out an actual repair operation and gave an airborne resin acid concentration of 70 µg/m³ over a sampling period of 3 minutes. Sample HPB04 was taken during an artificial soldering operation on an old PCB and gave an airborne resin acid concentration of 444 µg/m³ over a sampling period of 5 minutes. The two samples therefore had a total sampling time of 8 minutes, during which the mean airborne resin acid concentration was 304 µg/m³ ((444 x 5/8) + (70 x 3/8)).

The two low volume personal samples gave airborne concentrations of 16 µg/m³ (LPL01) and 41 µg/m³ (LPB02). Although derived from only one pair of samples, these results indicate that the filter located in the breathing zone collects around 2½ times as much resin acids as that located on the lapel. The concentrations for the two personal samples are time weighted averages over the whole sampling period of around 85 minutes, but the operative was only carrying out soldering operations for around 15 - 20 minutes of this (amounting to around 1/5th of the total sampling period). This means that the resin acid concentrations during the actual soldering period are about five times the levels quoted above, ie around 80 µg/m³ for the lapel sample and 200 µg/m³ for the breathing zone sample.

During the 15 - 20 minute soldering period the individual under test spent around half the time in actual soldering operations, and the other half desoldering the various components. The low flow rate breathing zone sample (LPB02) covers the whole of this 15 - 20 minute soldering/desoldering period and gives an estimated resin acid concentration of around 200 µg/m³. The two L60 breathing zone samples (HPB03 and HPB04) cover only the actual soldering period and give a mean resin acid concentration of around 300 µg/m³. Since it could be seen visually that the desoldering operations did not generate nearly as much fume as the soldering, this suggests that the results from the high and low flow rate breathing zone samples are reasonably consistent.

TABLE 26: TOTAL RESIN ACIDS COLLECTED ONTO SAMPLE FILTERS

SAMPLE NUMBER	SAMPLING VOLUME (m ³)	TOTAL RESIN ACID INJECTED (ng)			AIRBORNE RESIN ACID CONCENTRATION (µg/m ³)		
		DHA	ABI	TRA	DHA	ABI	TRA
LPL01	0.0850	0.55	0.75	3.50	2.52	3.50	16.11
LPB02	0.0829	1.18	2.78	8.55	5.57	13.35	40.85
HPB03	0.1575	3.20	11.08	27.60	8.15	28.41	70.34
HPB04	0.2675	34.10	121.93	297.38	50.94	182.31	444.26
HBG05	4.8015	1.10	2.10	9.75	0.04	0.16	0.41
HBG06	4.4260	0.53	0.18	4.80	0.00	0.00	0.03
HBG07	4.3650	0.40	0.15	4.43	0.00	0.00	0.00

7.2.2 Charcoal Tube Samples

Table 27 shows the amounts of the 3 main volatiles in 1 µl injections of the two sample solutions from the desorbed charcoal tubes calculated from the relative peak areas obtained in the GC analysis. From these values were obtained the airborne concentrations of the volatile components. Unlike the particulate fraction, the volatile concentration collected on the lapel and in the breathing zone sample are virtually identical. This suggests that the components sampled are uniformly distributed throughout the immediate work area, and in the case of xylene may not even emanate from the solder fume. The levels from all the volatile components are very low indeed.

TABLE 27: VOLATILES COLLECTED ON SAMPLE CHARCOAL TUBES

SAMPLE NUMBER	SAMPLING VOLUME (m ³)	VOLATILES INJECTED (ng)			AIRBORNE VOLATILES (µg/m ³)		
		Xylene	α-Pinene	Limonene	Xylene	α-Pinene	Limonene
LPL01	0.0850	4.04	1.10	0.15	23.7	6.5	0.9
LPB02	0.0829	3.78	1.04	0.13	22.8	6.3	0.8

7.3 FIELD TRIAL AT A TELEVISION REPAIR FACILITY (II)

The second field trial was carried out on the premises of a company repairing televisions, videos and other domestic audio-visual equipment on September 3rd 1992. The work area comprised a single room some 35 m long by 15 m wide, around half of which was used for the repair work, with the other half used for storage of the electrical goods before and after repair. On the day of the visit, three employees were involved in repair work requiring intermittent soldering operations. The three were seated at individual work stations, and were using unextracted hand-held soldering irons. The solder being used was CEL 60/40 BS219KP in 18 SWG and 22 SWG gauges, with the soldering irons of the three operators at temperatures of 320°C (Operator M), 280°C (Operator C) and 340°C (Operator D). During repair work, some desoldering was also necessary, and this was carried out with the help of a solder sucking wick which also contains flux. During the working day two of the three employees were soldering for approximately 3 - 5% of the time, and the other for around 10 - 15% of the time.

A total of 16 solder fume samples were taken onto Millipore-MF and DM800 membrane filters. These consisted of 6 low flow rate personal samples (3 pairs of lapel/breathing zone samples), 5 high flow rate personal samples and 5 high flow rate background samples. The locations of the various samplers are shown in Figure 12, and sampling details given in Table 28.

FIGURE 12: FIELD TRIAL 2 WORK-PLACE FLOOR PLAN & SAMPLING LOCATIONS

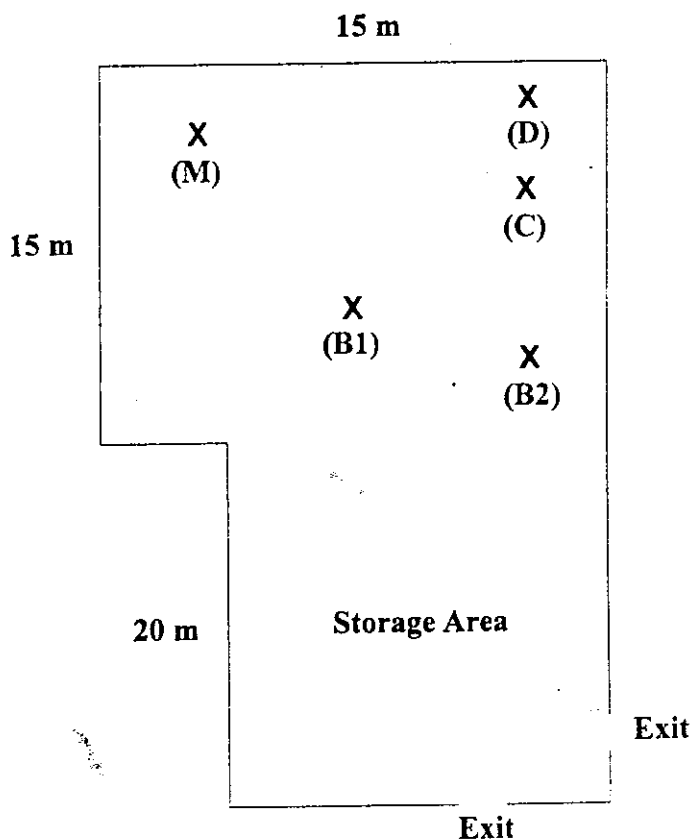


TABLE 28: SAMPLING DETAILS FROM FIELD TRIAL 2

SAMPLE NUMBER	FILTER TYPE	SAMPLING LOCATION	SAMPLING RATE (l/min)	SAMPLING TIME (mins)	SAMPLE VOLUME (m ³)
LPL08	SMWP	Operator M (Lapel)	0.94	244	0.229
LPB09	SMWP	Operator M (B-Zone)	0.95	244	0.233
LPL10	SMWP	Operator C (Lapel)	0.96	295	0.283
LPB11	SMWP	Operator C (B-Zone)	0.95	295	0.280
LPL12	SMWP	Operator D (Lapel)	0.97	285	0.275
LPB13	SMWP	Operator D (B-Zone)	0.97	285	0.276
HPB14	DM800	Operator D (B-Zone)	46.0	8	0.368
HPB15	DM800	Operator D (B-Zone)	56.0	17	0.952
HPB16	DM800	Operator D (B-Zone)	56.0	10	0.560
HPB17	DM800	Operator M (B-Zone)	54.7	7	0.383
HPB18	DM800	Operator M (B-Zone)	52.0	11	0.572
HBG19	DM800	Bench 1 (ca. 10 ft from Soldering)	42.4	33	1.399
HBG20	DM800	Bench 1 (ca. 10 ft from Soldering)	55.0	120	6.594
HBG21	DM800	Bench 1 (ca. 10 ft from Soldering)	56.0	120	6.720
HBG22	DM800	Bench 1 (ca. 10 ft from Soldering)	53.5	75	4.013
HBG23	DM800	Bench 2 (ca. 10 ft from Soldering)	54.3	227	12.320

7.3.1 Filter Samples

The sample chromatograms showed a number of peaks with a retention time of between 5 and 10 minutes in addition to those attributable to the presence of resin acids, including some which caused significant interference, particularly for those samples with very low resin acid concentrations. Sample blanks for both the personal and L60 samples were therefore analysed, and their results subtracted from those of the sample filters. Separate blanks were used for the personal and L60 samples because of the different filter materials used in the two cases.

Table 29 shows the amount of total resin acid in a 1 µl injection of each of the sixteen sample solutions calculated from the relative peak areas obtained in the GC analysis. The table also gives the airborne total resin acid concentration obtained from these concentration after correction with an appropriate blank.

The results in Table 29 indicate a 4-hr (roughly) TWA concentration of airborne resin acids in the personal samples of 2 - 12 µg/m³. In all three cases the breathing zone sample is higher than the lapel sample (by between 2 and 5 times). It was estimated that Operators M and C were soldering for about 5% of the sampling period and Operator D for about 12%. This gives breathing zone resin acid concentrations, whilst soldering, for the three operators estimated as around 200 µg/m³ for Operator M, 120 µg/m³ for Operator C and 105 µg/m³ for Operator D. However, it is likely that these figures are over-estimates because of the significant 1 - 5 µg/m³ background level of resin acids determined from the five background L60 samples HBG19 to HGB23.

The three short term breathing zone samples for Operator D showed levels of around 35, 45 and 120 µg/m³. The first two figures are significantly lower than the 105 µg/m³ estimated from the low flow rate samplers, although the third figure is more consistent. It is not clear why the third L60 sample should be three times higher than the other two, since the tasks being carried out in each case seemed very similar.

The two short term breathing zone samples for Operator M showed levels of around 4 and 40 µg/m³. The reason for the difference in the two samples is that very little soldering was done whilst the first sample was being taken. As was the case with Operator D, the L60 concentrations are much lower than the 200 µg/m³ estimate obtained above from the low flow rate breathing zone samples.

TABLE 29: TOTAL RESIN ACIDS COLLECTED ONTO SAMPLE FILTERS

SAMPLE NUMBER	OPERATOR NAME	TOTAL RESIN ACID INJECTED (ng)			AIRBORNE RESIN ACID CONCENTRATION ($\mu\text{g}/\text{m}^3$)		
		DHA	ABI	TRA	DHA	ABI	TRA
LPL08	M	0.33	0.14	1.07	0.58	0.24	1.87
LPB09	M	1.52	2.00	5.59	2.61	3.43	9.60
LPL10	C	0.62	0.06	1.39	0.87	0.08	1.96
LPB11	C	1.05	1.28	3.98	1.50	1.83	5.68
LPL12	D	1.18	0.75	4.05	1.71	1.09	5.87
LPB13	D	2.45	3.04	8.60	3.56	4.42	12.51
HPB14	D	25.67	31.70	105.15	10.78	13.31	44.18
HPB15	D	44.86	56.34	171.85	32.04	40.24	122.75
HPB16	D	7.68	13.76	33.04	8.35	14.96	35.91
HPB17	M	1.81	1.05	4.15	1.89	1.10	4.33
HPB18	M	13.86	23.28	59.81	9.69	16.28	41.82
HBG19	Background	5.89	5.06	16.42	1.68	1.45	4.69
HBG20	Background	29.93	12.71	83.86	1.82	0.77	5.06
HBG21	Background	5.46	6.51	19.34	0.32	0.39	1.15
HBG22	Background	4.58	6.66	17.86	0.46	0.66	1.78
HBG23	Background	13.52	17.52	47.33	0.44	0.57	1.54

7.3.2 Gravimetric Analysis

The L60 sample filters, together with a number of blanks, were weighed before and after sampling to obtain a figure for total dust sampled. The results are shown in Table 30, together with the corresponding TRA concentration obtained from the GC analysis above. Such a comparison suggests although total dust concentration may provide some indication of TRA concentration within a given work area, the relationship between the two is not linear.

TABLE 30: GRAVIMETRIC ANALYSIS OF L60 SAMPLE FILTERS.

SAMPLE NUMBER	OPERATOR NAME	FILTER WEIGHT (mg)		TOTAL DUST (μg)		T-DUST ($\mu\text{g}/\text{m}^3$)	TRA ($\mu\text{g}/\text{m}^3$)
		BEFORE	AFTER	ABSOLUTE	- BLANK		
Blank	---	32.080	31.975	-105.	0	0	0.0
HPB14	D	32.765	32.920	155	260	273	44.2
HPB15	D	33.030	33.140	110	215	384	122.8
HPB16	D	35.590	35.550	-40	65	177	35.9
HPB17	M	31.500	31.450	-60	45	117	4.3
HPB18	M	35.210	35.250	50	155	271	41.8
HBG19	Background	44.630	44.650	20	125	89	4.7
HBG20	Background	30.760	31.300	540	645	98	5.1
HBG21	Background	30.030	30.430	400	505	75	1.2
HBG22	Background	33.220	33.410	190	295	74	1.8
HBG23	Background	29.420	30.090	670	775	63	1.5

7.3.3 Charcoal Tube Samples

Table 31 shows the amounts of the 4 main volatiles in 1 µl injections of the six sample solutions from the desorbed charcoal tubes. These values were calculated from the relative peak areas obtained in the GC analysis, and were used to calculate the corresponding airborne concentrations of the volatile components.

A comparison of volatile concentrations obtained on the lapel and in the breathing zone for the three operators produced the following observations.

- Toluene, xylene, α-pinene and limonene concentrations for Operators M and D are roughly twice as high on the lapel as in the breathing zone.
- Toluene, α-pinene and limonene concentrations for Operator C were similar for both sampling locations, however xylene concentration is roughly twice as high on the lapel as in the breathing zone.
- The lapel and breathing zone concentrations of toluene, xylene, α-pinene and limonene for all three operators are very low in comparison with their respective OESs.

TABLE 31: VOLATILES COLLECTED ON SAMPLE CHARCOAL TUBES

SAMPLE NUMBER	OPERATOR NAME	VOLATILES INJECTED (ng)				AIRBORNE VOLATILES (µg/m ³)			
		Toluene	Xylene	α-Pinene	Limonene	Toluene	Xylene	α-Pinene	Limonene
LPL08	M	91.1	30.1	6.4	45.8	199.0	65.8	14.0	100.0
LPB09	M	47.5	11.6	3.3	27.3	102.0	24.9	7.1	58.6
LPL10	C	47.0	20.4	4.0	22.9	83.0	36.1	7.1	40.4
LPB11	C	43.7	11.5	3.6	21.8	78.0	20.5	6.5	39.0
LPL12	D	123.7	31.2	6.7	51.7	224.0	56.6	12.2	93.7
LPB13	D	60.5	15.0	3.9	28.7	110.0	27.3	7.0	52.1

7.4 FIELD TRIAL AT AN ELECTRICAL COMPONENTS MANUFACTURER

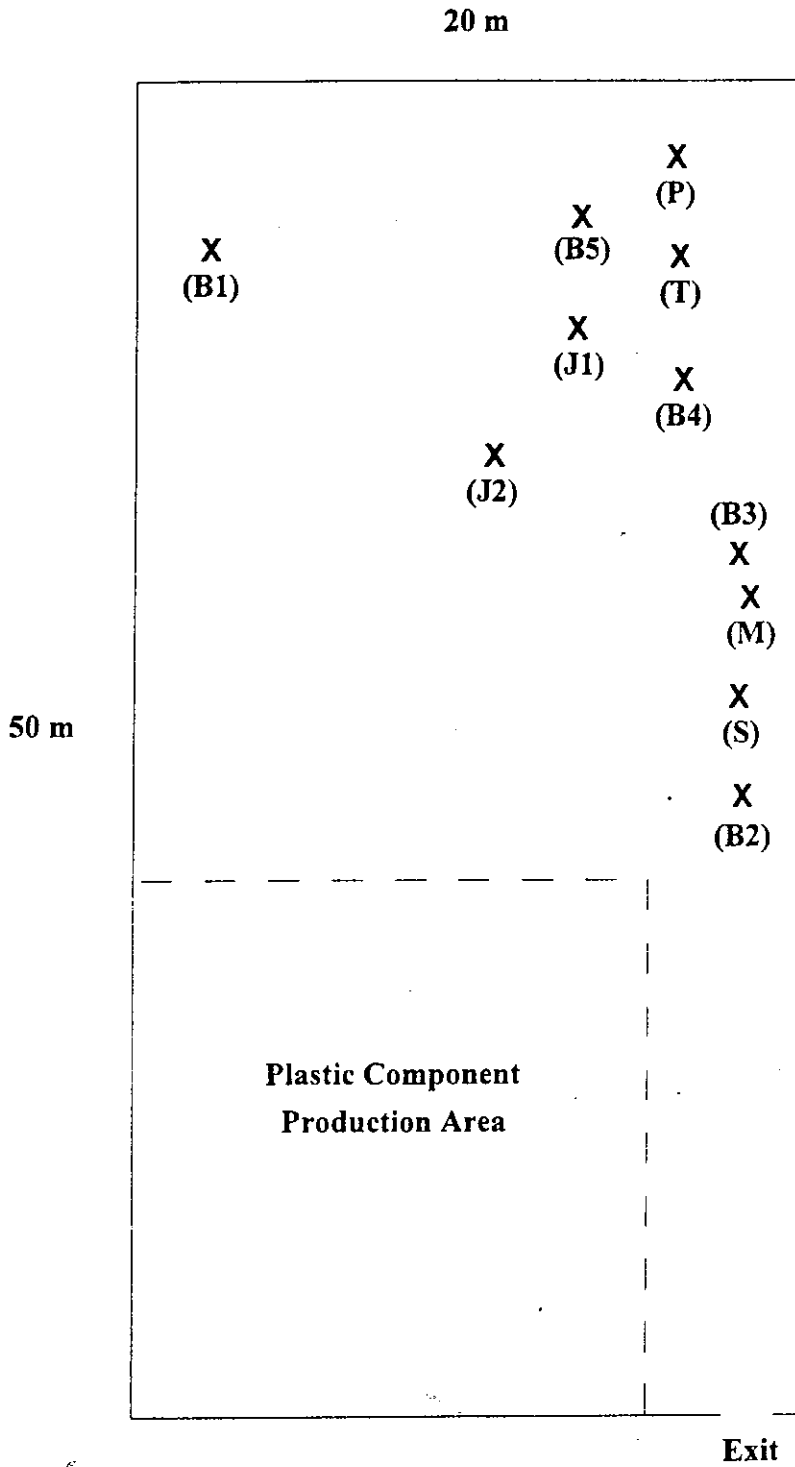
The third field trial was carried out on the premises of a company manufacturing electrical components and windings for a number of domestic products on September 9th 1992. The work area comprised a single room some 50 m long by 20 m wide, around half of which was used for the manufacturing work. The other half of the work area was used for storage and producing plastic parts for the components - a process which appeared to release significant quantities of xylene into the workplace atmosphere.

On the day of the visit, between six and eight employees were involved in various soldering operations at any one time, using either hand-held soldering irons, solder pots or automatic tinning machines. Most were seated at individual benches, and the operations for the most part had no form of extraction - the exception being the automatic tinning machines which appeared to have some form of small filter extraction system. The ventilation to the building as a whole appeared limited, with just an open door at one end and an extractor fan set around 6 m up the wall at the other. There was little or no extraction of the solvents being used in the production of the plastic components on the site.

The solder used with the hand held soldering irons was described on the reel as 22 SWG Savbit DTD 599A 362 flux. For those operations employing the use of a solder pot, the flux was applied as a liquid to the components before dipping into the hot solder.

A total of 29 solder fume samples were taken onto Millipore-MF and DM800 membrane filters. These consisted of 10 low flow rate personal samples (5 pairs of lapel/breathing zone samples), 12 high flow rate personal samples and 7 high flow rate background samples. The locations of the various samplers are shown in Figure 13, and sampling details given in Table 32.

FIGURE 13: FIELD TRIAL 3 WORK-PLACE FLOOR PLAN & SAMPLING LOCATIONS



- P** = Operator P (Using Auto-tinner with fan/extractor at 420°C)
- T** = Operator T (Using Auto-tinner with fan/extractor at 420°C)
- J1** = Operator J1 (Using solder pot at 380°C with no flux)
- M** = Operator M (Hand soldering with 22 SWG Savbit DTD 599A 362 flux at 380°C)
- S** = Operator S (Using solder pot at 380°C with liquid flux)
- J2** = Operator J2 (Using solder pot at 380°C with liquid flux)

TABLE 32: SAMPLING DETAILS FROM FIELD TRIAL 3

SAMPLE NUMBER	FILTER TYPE	SAMPLING LOCATION	SAMPLING RATE (l/min)	SAMPLING TIME (mins)	SAMPLE VOLUME (m ³)
LPL24	SMWP	Operator P (Lapel)	0.96	194	0.187
LPB25	SMWP	Operator P (B-Zone)	0.94	194	0.183
LPL26	SMWP	Operator T (Lapel)	0.93	247	0.229
LPB27	SMWP	Operator T (B-Zone)	0.94	247	0.233
LPL28	SMWP	Operator J1 (Lapel)	0.99	283	0.279
LPB29	SMWP	Operator J1 (B-Zone)	0.94	283	0.265
LPL30	SMWP	Operator M (Lapel)	0.96	269	0.260
LPB31	SMWP	Operator M (B-Zone)	0.97	269	0.261
LPL32	SMWP	Operator J2 (Lapel)	0.99	259	0.256
LPB33	SMWP	Operator J2 (B-Zone)	0.95	259	0.246
HPB34	DM800	Operator J1 (B-Zone)	53.0	10	0.530
HPB35	DM800	Operator J1 (B-Zone)	63.5	10	0.635
HPB36	DM800	Operator J1 (B-Zone)	62.0	10	0.620
HPB37	DM800	Operator J1 (B-Zone)	60.5	10	0.605
HPB38	DM800	Operator S (B-Zone)	52.0	11	0.572
HPB39	DM800	Operator S (B-Zone)	61.0	10	0.610
HPB40	DM800	Operator T (B-Zone)	65.5	11	0.721
HPB41	DM800	Operator T (B-Zone)	62.0	6	0.372
HSB42	DM800	Operator M (B-Zone)	64.5	10	0.645
HPB43	DM800	Operator M (B-Zone)	62.5	10	0.625
HPB44	DM800	Operator P (B-Zone)	62.0	10	0.620
HPB45	DM800	Operator J2 (B-Zone)	64.0	10	0.640
HBG46	DM800	Bench 1 (ca. 20 ft from Soldering)	42.5	86	3.655
HBG47	DM800	Bench 1 (ca. 20 ft from Soldering)	47.0	236	11.092
HGB48	DM800	Bench 2 (ca. 4 ft from Soldering)	51.0	314	16.014
HGB49	DM800	Bench 3 (ca. 4 ft from Soldering)	44.0	61	2.684
HGB50	DM800	Bench 3 (ca. 4 ft from Soldering)	45.0	211	9.495
HGB51	DM800	Bench 4 (ca. 3 ft from Soldering)	48.5	263	12.756
HGB52	DM800	Bench 5 (ca. 2 ft from Soldering)	60.5	13	0.787

7.4.1 Filter Samples

As before, the sample chromatograms showed a number of interfering peaks in the resin acid region with retention times between 5 and 10 minutes. Sample blanks for both the personal and L60 samples were therefore analysed, and their results subtracted from those of the sample filters. Separate blanks were used for the personal and L60 samples because of the different filter materials used in the two cases.

Table 33 shows the amounts of total resin acid in 1 µl injections of each of the twenty-nine sample solutions calculated from the relative peak areas obtained in the GC analysis. The table also gives the airborne total resin acid concentration obtained from these concentration after correction with an appropriate blank.

The results in Table 33 indicate a 4-hr (roughly) TWA concentration of airborne resin acids of around 8 - 100 $\mu\text{g}/\text{m}^3$. Four of the five solderers show fairly similar exposures of between 8 and 20 $\mu\text{g}/\text{m}^3$, whilst Operator M is significantly higher at around 100 $\mu\text{g}/\text{m}^3$ for both the lapel and breathing zone samples.

Comparison of the lapel and breathing zone samples in Table 33, shows that in two of the five pairs, the breathing zone sample is significantly higher than the lapel (by 55 - 90%). However, in the other three pairs there appears to be little difference between the two sampling positions. This could be due to the relatively high background concentration of resin acids (between 6 and 20 $\mu\text{g}/\text{m}^3$ depending on location), which is similar to the levels obtained in several of the personal samples, thus making the positioning of the personal sampler on the operative of much less importance.

TABLE 33: TOTAL RESIN ACIDS COLLECTED ONTO SAMPLE FILTERS

SAMPLE NUMBER	OPERATOR NAME	TOTAL RESIN ACID INJECTED (ng)			AIRBORNE RESIN ACID CONCENTRATION ($\mu\text{g}/\text{m}^3$)		
		DHA	ABI	TRA	DHA	ABI	TRA
LPL24	P	1.52	0.42	3.84	3.25	0.90	8.22
LPB25	P	2.03	2.62	4.21	4.44	1.35	9.20
LPL26	T	2.19	1.75	6.20	3.83	3.06	10.85
LPB27	T	4.86	1.98	12.00	8.34	3.40	20.60
LPL28	J1	3.25	1.12	9.31	4.66	1.61	13.35
LPB29	J1	5.69	1.87	13.65	8.54	2.82	20.60
LPL30	M	16.62	18.36	58.99	25.45	28.11	90.33
LPB31	M	20.23	20.08	66.17	31.15	30.92	101.88
LPL32	J2	3.22	2.26	8.57	5.03	3.53	13.39
LPB33	J2	4.10	1.19	8.51	6.68	1.94	13.87
HPB34	J1	5.33	3.43	13.99	4.02	2.59	10.56
HPB35	J1	1.64	2.96	10.36	1.03	1.86	6.52
HPB36	J1	1.00	1.57	3.92	0.65	1.01	2.53
HPB37	J1	3.17	3.00	9.09	2.10	1.98	6.01
HPB38	S	41.97	21.95	107.58	29.35	15.35	75.23
HPB39	S	13.05	3.61	28.47	8.55	2.37	18.67
HPB40	T	7.06	7.26	21.93	3.92	4.03	12.18
HPB41	T	0.49	0.34	1.81	0.53	0.36	1.94
HPB42	M	6.13	3.20	17.62	3.04	1.59	8.74
HPB43	M	6.94	9.92	25.90	4.44	6.35	16.58
HPB44	P	1.63	1.39	4.48	1.05	0.90	2.89
HPB45	J2	0.85	1.47	3.06	0.53	0.92	1.91
HBG46	Background	33.31	23.50	95.97	3.64	2.57	10.50
HBG47	Background	59.58	57.04	203.89	2.15	2.06	7.35
HBG48	Background	138.69	169.05	537.12	3.47	4.22	13.42
HBG49	Background	37.40	43.65	130.81	5.57	6.51	19.50
HBG50	Background	41.58	38.97	140.36	1.75	1.64	5.91
HBG51	Background	67.71	45.67	202.19	2.12	1.43	6.34
HBG52	Background	2.26	1.00	5.03	1.15	0.51	2.56

The TWA figure for Operator M of 100 $\mu\text{g}/\text{m}^3$ appears somewhat high when compared with her two L60 personal samples (HPB42 & HPB43) which gave levels of 9 - 16 $\mu\text{g}/\text{m}^3$. It can only be assumed that the personal L60 samplers were not representative of Operator Ms exposure over the whole sampling period, since contamination of the samplers seems unlikely as both the lapel and breathing zone samples gave similarly high results. It may be significant that the two L60 breathing zone samples taken on Operator S sitting at the adjoining bench also showed wide variation. Samples HPB39 (Operator S) and HPB43 (Operator M) were taken one after the other at around 2.15 pm and show very similar TRA concentration of around 16 $\mu\text{g}/\text{m}^3$. Sample HPB38 (Operator S) taken at around 10.45 am showed a much higher concentration of 75 $\mu\text{g}/\text{m}^3$, a figure which is more consistent with Operator Ms overall TWA result, whereas sample HPB42 (Operator M) taken at around 11.45 am is slightly lower at around 9 $\mu\text{g}/\text{m}^3$.

This wide variation of personal exposures for Operators S and M seem to suggest the presence of an intermittent source of solder fume which causes a temporary, but large, increase in local solder fume concentration. The identity of this source remains unknown, although it may be worth noting that Operator M was the only person using a hand held soldering iron.

It was also observed that several L60 personal samples taken just before (around 12.15 pm) and just after (around 1.30 pm) the lunch break seem lower than those taken at other times, although again the reasons for this are unclear.

7.4.2 Gravimetric Analysis

The L60 sample filters, together with blanks, were weighed before and after sampling to obtain a figure for total dust sampled. The results are shown in Table 34, with the corresponding TRA concentration obtained by GC analysis. Comparison of the results suggests that the relationship between total dust concentration and TRA concentration within the given work area is not linear.

TABLE 34: GRAVIMETRIC ANALYSIS OF L60 SAMPLE FILTERS

SAMPLE NUMBER	OPERATOR NAME	FILTER WEIGHT (mg)		TOTAL DUST (μg)		T-DUST ($\mu\text{g}/\text{m}^3$)	TRA ($\mu\text{g}/\text{m}^3$)
		BEFORE	AFTER	ABSOLUTE	- BLANK		
Blank	---	32.080	31.975	-105	0	0	0.0
HPB34	J1	37.420	37.600	180	135	255	10.6
HPB35	J1	36.095	36.550	455	410	646	6.5
HPB36	J1	30.610	30.750	140	95	153	2.5
HPB37	J1	34.850	35.040	190	145	240	6.0
HPB38	S	35.280	35.540	260	215	376	75.2
HPB39	S	32.970	33.100	130	85	139	18.7
HPB40	T	30.410	30.540	130	85	118	12.2
HPB41	T	36.130	36.210	80	35	94	1.9
HPB42	M	30.285	30.420	135	90	112	8.7
HPB43	M	34.130	34.265	135	90	144	16.6
HPB44	P	33.200	33.310	110	65	105	2.9
HPB45	J2	38.460	38.560	100	55	86	1.9
HGB46	Background	40.610	41.270	660	615	168	10.5
HGB47	Background	33.210	35.960	2750	2705	244	7.4
HGB48	Background	31.750	35.730	3980	3935	246	13.4
HGB49	Background	40.400	41.140	740	695	259	19.5
HGB50	Background	34.910	37.580	2670	2625	276	5.9
HGB51	Background	33.890	36.350	2460	2415	189	6.3
HGB52	Background	37.475	37.600	125	80	102	2.6

7.4.3 Charcoal Tube Samples

Table 35 shows the amounts of the 4 main volatiles in 1 µl injections of the six sample solutions from the desorbed charcoal tubes. These values were calculated from the relative peak areas obtained in the GC analysis, and were used to calculate the corresponding airborne concentrations of the volatile components.

The airborne concentrations of the volatiles components collected on the lapel and in the breathing zone are very similar, suggesting that the components sampled are uniformly distributed throughout the work area. In the case of xylene, the source is the area producing the plastic components and not the solder. All the components with the exception of xylene were present in very low concentrations in comparison with their OES.

TABLE 35: VOLATILES COLLECTED ON SAMPLE CHARCOAL TUBES

SAMPLE NUMBER	OPERATOR NAME	VOLATILES INJECTED (ng)				AIRBORNE VOLATILES (µg/m ³)			
		Toluene	Xylene	α-Pinene	Limonene	Toluene	Xylene	α-Pinene	Limonene
LPL24	P	6.7	20234	17.6	9.7	18	54100	47	26
LPB25	P	10.6	18549	18.7	3.3	29	50680	51	9
LPL26	T	44.9	29300	27.5	0.5	98	63970	60	1
LPB27	T	26.1	27469	16.8	3.3	56	58950	36	8
LPL28	J1	15.1	36316	41.3	1.1	27	65080	74	2
LPB29	J1	14.3	31284	36.0	3.7	27	59030	68	7
LPL30	M	28.6	51291	61.9	2.1	55	98640	119	4
LPB31	M	19.8	46925	56.4	2.6	38	89890	108	5
LPL32	J2	110.2	27049	41.5	1.5	20	52830	81	3
LPB33	J2	10.3	27802	42.8	0.4	21	56510	87	1

8. CONCLUSIONS & RECOMMENDATIONS

The present method for determining levels of solder fume is based on measurement of aldehydic pyrolysis products (quoted as formaldehyde). However, such aldehydes make up only around 0.1% of the total fume and as such require the use of extremely sensitive methods, particularly if short sampling times are required. Additionally, there are many potential sources of formaldehyde in a factory environment other than solder fume, and it is therefore not uncommon for the correlation between aldehyde concentration and the levels of solder fume to be quite poor^(6,13).

For this reason an investigation has been carried out into the sampling and analysis of all the various volatile and particulate fractions of solder. This report details that investigation, the main conclusion of which is that measurement of total airborne resin acids offers a suitable method for determining the solder fume content of a given atmosphere. These resin acids are generated from the heated rosin flux, and form the major part of the fume (around 90%). In addition, unlike formaldehyde, such resin acids are likely to originate only from the flux and are therefore not subject to interference from outside sources.

Resin acids are present in the fume as a particulate and were therefore collected by passing the air sample through a membrane filter. Once collected, a method of qualitative and quantitative analysis based on methylation followed by gas chromatography was developed. In most air samples, seven or eight distinct resin acids could be separated and quantified. The total resin acid content of the air sample could then be quoted as well as that for any of the individual resin acids, such as abietic or dehydroabietic acid.

Variations were found to occur in the ratios of the resin acids present in fume generated from different solder types, and it is probably therefore advisable for quantification purposes to measure the total resin acid concentration present rather than that for any individual resin acid. An additional reason for this approach is that there appears to be little agreement at present as to which, if any, of the resin acids in the fume is the cause of the respiratory problems observed.

Although it is being proposed that the future OES for solder fume will be based on measurement of resin acid, it has not yet been decided at what concentration the limit will be set, although figures of 100 - 200 $\mu\text{g}/\text{m}^3$ have been suggested. The method outlined in this report has sufficient sensitivity to cope with an OES of this order as this investigation has suggested the following detection limits can be achieved using high and low flow rate samplers.

- a) 1 l/min samples - 51 $\mu\text{g}/\text{m}^3$ for a 10 minute sample.
 - 34 $\mu\text{g}/\text{m}^3$ for a 15 minute sample.
 - 1.4 $\mu\text{g}/\text{m}^3$ for a 360 minute sample.
- b) 50 l/min samples - 1.0 $\mu\text{g}/\text{m}^3$ for a 10 minute sample.
 - 0.7 $\mu\text{g}/\text{m}^3$ for a 15 minute sample.
 - 0.03 $\mu\text{g}/\text{m}^3$ for a 360 minute sample.

Previously most samplers have tended to be sited on the lapel of the individual under test, however for a highly directional problem such as solder fume this location may not always give a true assessment of a workers personal exposure. On generation, solder fume tends to rise as an almost vertical plume from the heat source, thus fume concentrations are therefore far from uniform throughout the immediate work area. Inside, or close to, the main plume the fume concentrations can be extremely high, whereas away from the plume the levels are much lower. Consequently, sampling equipment necessary for more representative assessment of personal exposure to solder fume has also been developed.

Since most hand soldering is done seated at bench level, it is usually the case that the plume tends to be directed towards the area of the breathing zone rather than that of the lapel, making it highly likely that the solder fume concentration will be highest in the breathing zone. This is made all the more significant by the fact that solder fume is a respiratory sensitiser, and it is therefore essential for accurate assessment of personal exposure that the sampling device should be sited as close as possible to the breathing zone. With this in mind, the smallest possible sampling head has been used in order that it can be conveniently sited in the breathing zone on a modified pair of safety spectacles. During a series of field trials involving paired filter samplers, in almost every case those samplers located in the breathing zone showed higher resin acid concentrations than those sited in the conventional lapel position. It is therefore recommended that where possible all future solder fume sampling should be carried out with sampling heads sited in such a manner in the breathing zone.

Throughout the field trials, the low flow-rate personal samplers consisted of a filter and charcoal tube connected in series, enabling both particulate and volatile fractions of the fume to be collected. However, the volatiles detected provided little indication of the actual levels of solder fume present, since the levels were extremely low and often swamped by volatiles generated from other processes in the factory environment. For this reason it is recommended that charcoal tubes are eliminated from future solder fume sampling unless it is required to sample for some specific volatile component in addition to the solder fume. By removing the charcoal tube from the sampling equipment, the back-pressure is significantly reduced (see Table 17) which allows the maximum sampling rate to be increased from 1 to 2 l/min, with the following reductions in detection limit for 10 and 15 minute short-term samples.

- 26 $\mu\text{g}/\text{m}^3$ for a 10 minute sample (reduced from 51 $\mu\text{g}/\text{m}^3$).
- 17 $\mu\text{g}/\text{m}^3$ for a 15 minute sample (reduced from 34 $\mu\text{g}/\text{m}^3$).

The limits above are based on a final solution volume of 300 μl , but with suitable low volume vials this could be reduced to 150 μl with the following reductions in detection limit for 10 and 15 minute short-term samples (2 l/min sampling rate).

- 13 $\mu\text{g}/\text{m}^3$ for a 10 minute sample (reduced from 26 $\mu\text{g}/\text{m}^3$).
- 9 $\mu\text{g}/\text{m}^3$ for a 15 minute sample (reduced from 17 $\mu\text{g}/\text{m}^3$).

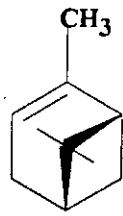
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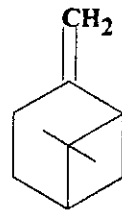
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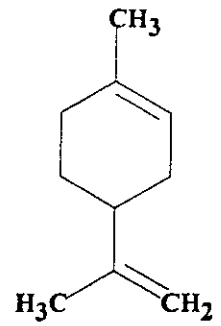
APPENDIX 1: MONO- AND SESQUITERPENES FOUND IN SOLDER FUME



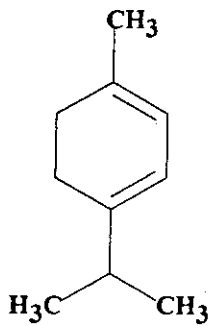
α -PINENE



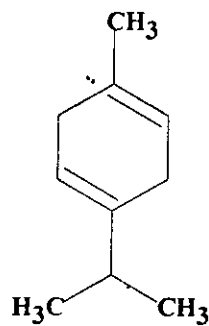
β -PINENE



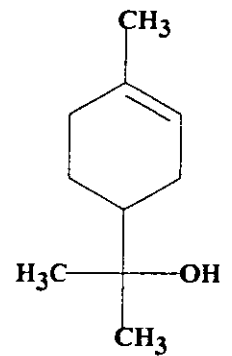
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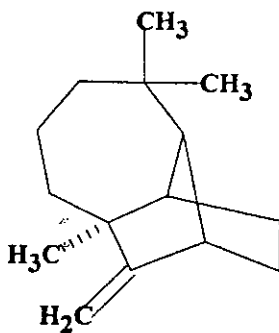
α -TERPINENE



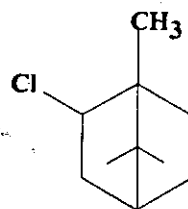
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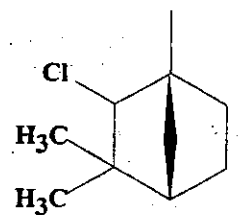
α -TERPINEOL



LONGIFOLENE

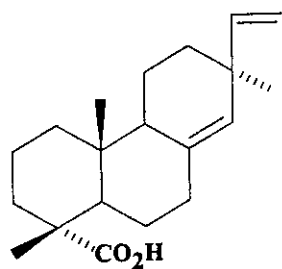


BORNYL CHLORIDE

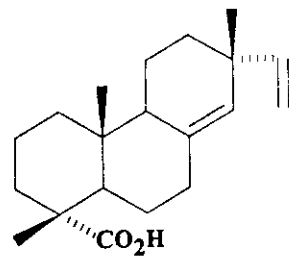


FENCHYL CHLORIDE

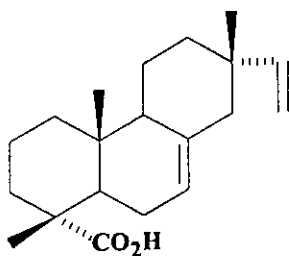
APPENDIX 2: RESIN ACIDS FOUND IN ROSIN



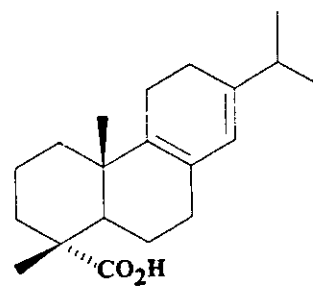
PIMARIC ACID



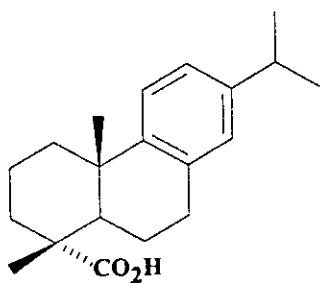
SANDARACOPIMARIC ACID



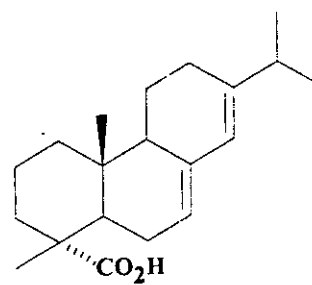
ISOPIMARIC ACID



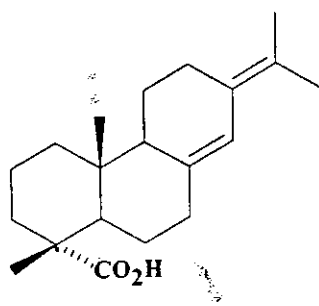
PALUSTRIC ACID



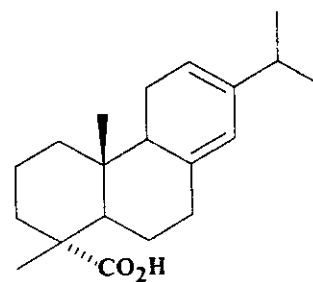
DEHYDROABIETIC ACID



ABIETIC ACID



NEOABIETIC ACID



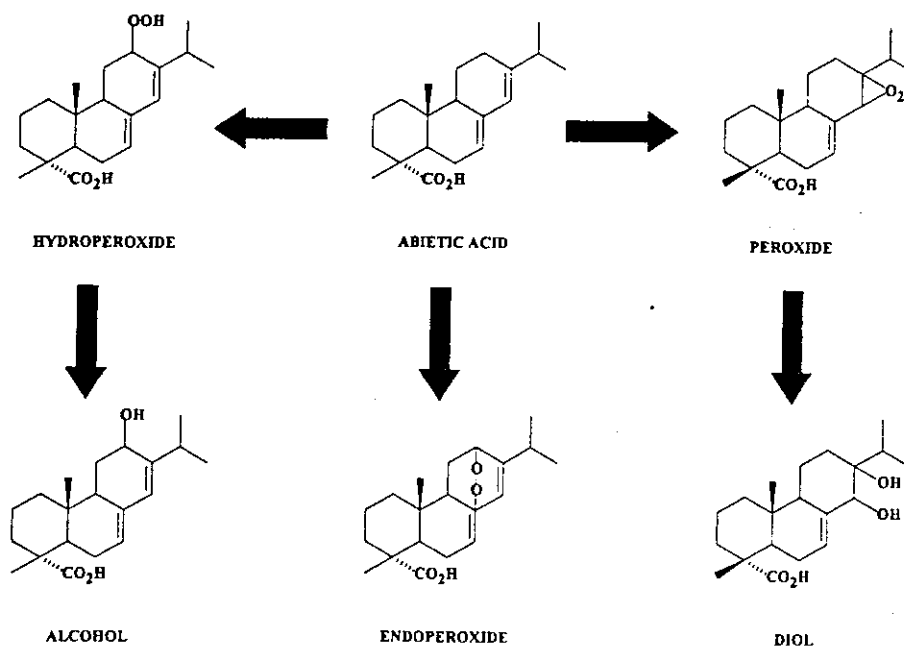
LEVOPIMARIC ACID

APPENDIX 3: OXIDATION OF RESIN ACIDS

Rozmej, Foks & Kwiatkowski suggest two mechanisms for the oxidation of resin acids which are illustrated in Figure A3.1, and are basically as follows⁽¹⁹⁾.

- Oxidation occurs from oxygen attaching to the double bonds forming peroxides and hydroperoxides. Such a process is supported by the drop in maximum absorption in the UV/VIS spectrum of abietic acid and colophony during oxidation as the result of the breakdown of the conjugated double bonds.
- Oxidation occurs by formation of hydroxyl groups in the alpha position to the double bond. This process is supported by visual observations in which the colophony is seen to darken - a process which occurs when double bonds in the para-quinone position remain unbroken. However, this suggestion that the double bonds remain unbroken appears to contradict the spectroscopic evidence above, and so the first mechanism may be the more likely.

FIGURE A3.1: MECHANISM FOR OXIDATION OF ABIETIC ACID

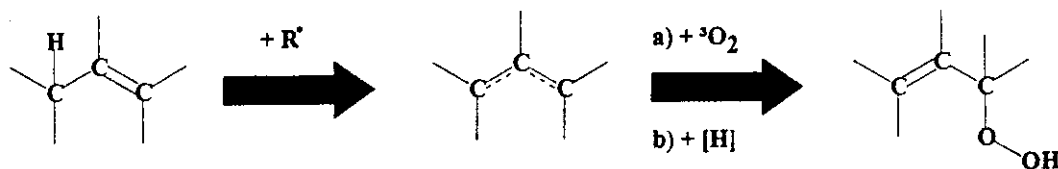


Soltes and Zinkel state that the yellowing of rosin has been attributed to oxidation which can occur when rosin or its derivatives are exposed to atmospheric oxygen for long periods, or to elevated temperatures in the presence of air⁽²⁰⁾. The oxidative stability of some rosins, both raw and heat/acid isomerised has been studied gravimetrically. In a powdered state these were found to gain 6-8% in weight in 90 days and 11-13% in five years. Rosins show weight gains which correlate with abietic acid content, with pure abietic acid gaining 23.5% in weight in five years.

Oxidation of rosin and oleorosin has been shown by ESR to be a free radical reaction in analogy with that for other unsaturated fatty acids and olefins, although structures for the free radicals were not put forward. The free radical chain reaction is similar to that of the typical example shown below.



Autoxidation can also occur via the dehydrogenation of an olefin by R^\cdot as shown below. This forms the delocalised free radical that subsequently reacts with triplet ground-state oxygen at the allylic position giving the appropriate peroxide.

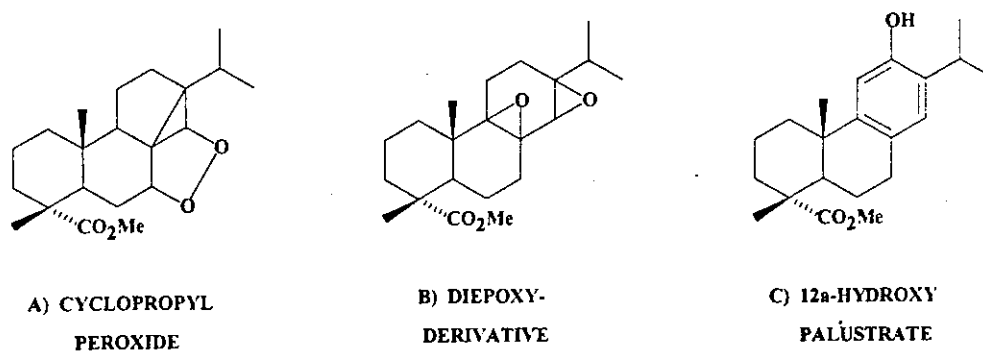


Pure levopimaric, palustric and neoabietic acids do not oxidise on exposure to air, but abietic acid rapidly gains weight and colour. Abietic acid autoxidation has been shown to proceed primarily by a free radical chain mechanism, accompanied by isomerization and oxidative decarboxylation.

Oxidative processes can also be induced photochemically to give a complex mixture of products. Air oxidation of methyl abietate in hexane under sunlight gives 7-oxo and hydroxy dehydroabietates, epoxy and hydroxy derivatives and a cyclopropyl peroxide (Figure A3.2A). Similar conditions with methyl palustrate gave 45% diepoxy derivatives (Figure A3.2B) along with 30% methyl dehydroabietate. Methyl levopimarate gave methyl esters of dehydroabietic, epoxy, epoxy-keto and epoxy-hydroxy acids. The formation of methyl dehydroabietate was attributed to the dehydration of the intermediate 12 α -hydroxypalustrate (Figure A3.2C). The formation of this intermediate helps to explain why non-polar solutions of methyl levopimarate, palustrate and 8,12-abietadienoate undergo oxidation/dehydration to dehydroabietate.

Dehydroabietic and pimaric/isopimaric acids are found to be much more resistant to air oxidation, and usually require the use of catalysts and/or oxidising reagents.

FIGURE A3.2: MISCELLANEOUS OXIDATION PRODUCTS OF RESIN ACIDS

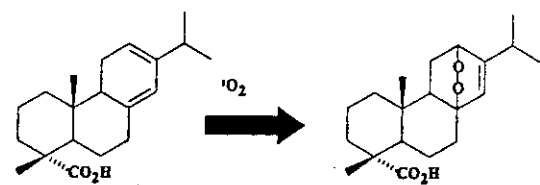


Photosensitized oxidation of levopimaric, palustric, neoabietic and abietic acids readily occurs at low temperature in a polar solvent such as ethanol and in the presence of a photoactivator such as rose bengal or methylene blue, to form endoperoxides (the reaction with abietic acid is slower than the other three). These reactions are illustrated in Figure A3.3.

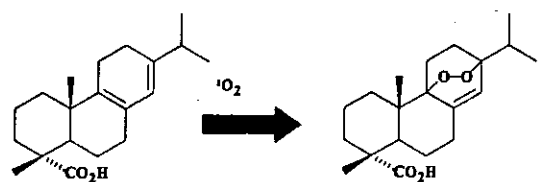
Schuller and Lawrence⁽²¹⁾ found the photosensitized oxidation of neoabietic acid to yield a crystalline diperoxide, determined as 18-hydroperoxy-6,14,peroxy-7⁽¹⁰⁾-dihydroabietic acid (Figure A3.4). Suitable blank experiments were carried which demonstrated that all three elements of air, light and dye were necessary for reaction. Pimaric, isopimaric and dehydroabietic acid were found to unreactive under the same conditions.

Table A3.1 shows the results of testing a number of compounds as photosensitisers for use in the photosensitized oxidation of resin acids.

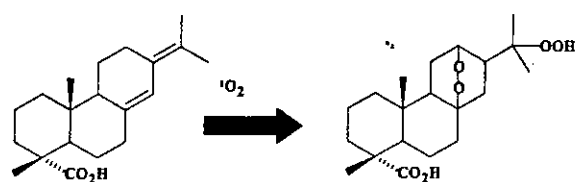
FIGURE A3.3: PHOTSENSITISED (SINGLET OXYGEN) OXIDATION OF ABIETADIENOIC ACIDS



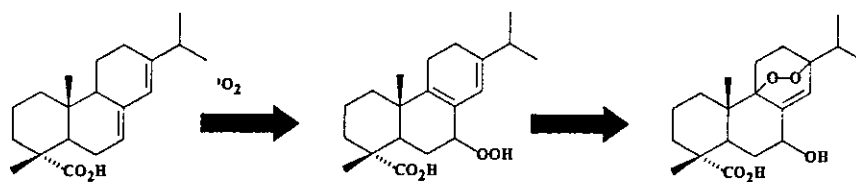
LEVOPIMARIC



PALUSTRIC



NEOABIETIC



ABIETIC

FIGURE A3.4: PHOTSENSITISED OXIDATION OF NEOABIETIC ACID

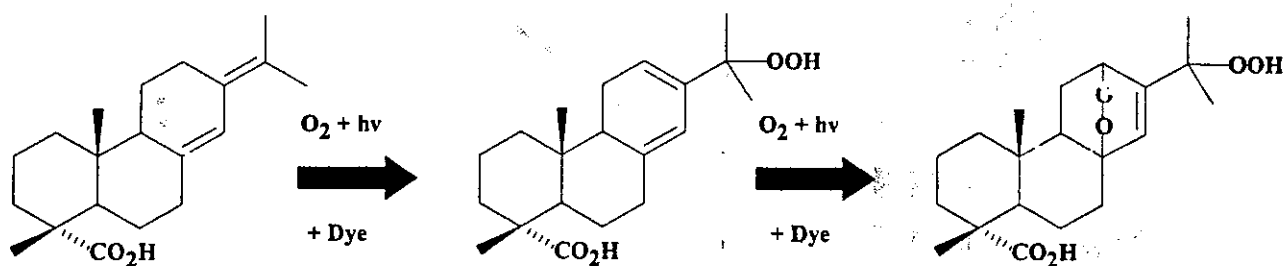


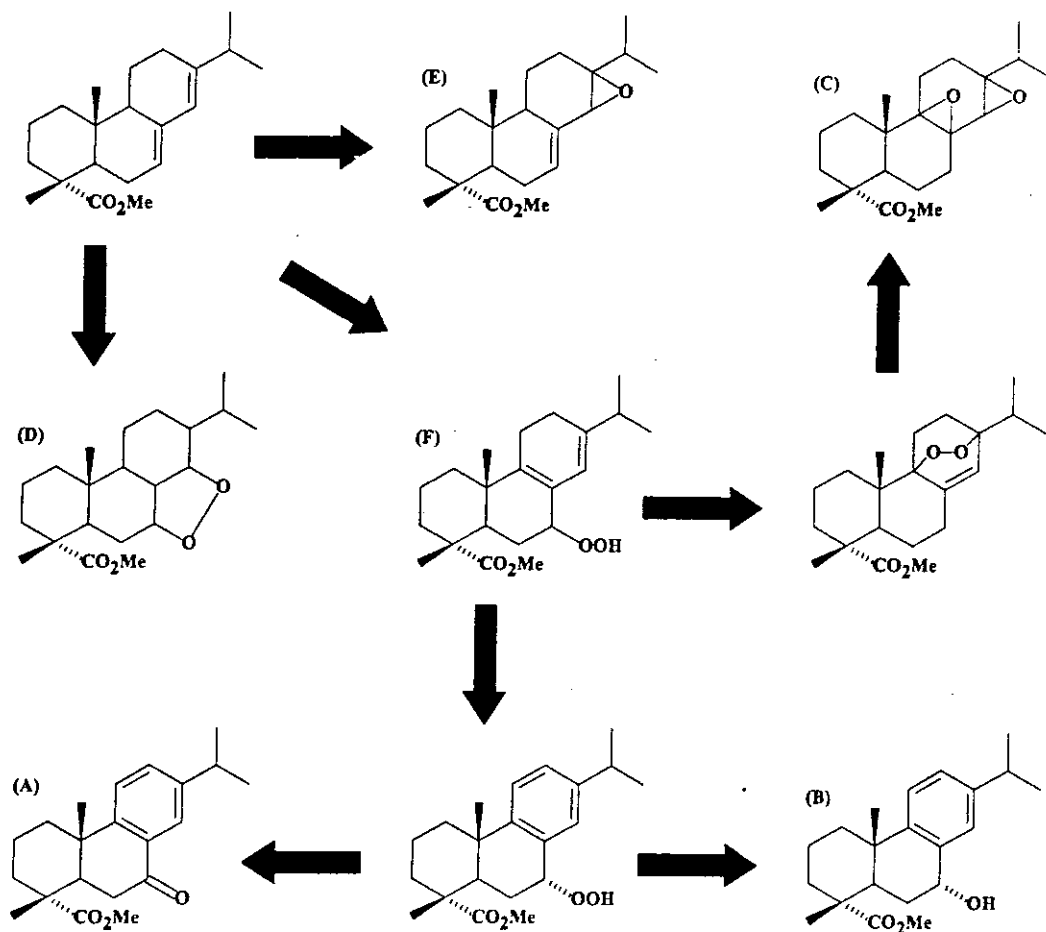
TABLE A3.1: TESTING OF PHOTSENSITISING DYES

PHOTOSENSITISING DYE	COLOUR OF THE ETHANOL SOLUTION	PERCENTAGE RESIN ACID REACTED IN 1 HOUR*		
		NEO	LEV	PAL
Rose Bengal	Red	53	58	64
Erythrosin B	Red	41	50	54
Methylene Blue	Blue	36	48	58
Chlorophyll	Green	34	46	48
Eosin YS	Orange	25	26	26
9,10-Anthraquinone	Colourless	25	---	---
Mecurochrome	Orange	19	---	---
1,4-Napthoquinone	Pale Yellow	10	---	---
9,10-Phenanthrenequinone	Yellow	6	---	---
Benzil	Colourless	4	---	---

* Resin Acid Concentration = 0.01 M, Dye Concentration = 50 mg/l.

Enoki and Kitao studied the process of autooxidation by subjecting methyl abietate to irradiation with sun light in air⁽²²⁾. Five n-hexane soluble products were isolated from the reaction (Figure A3.5) and identified as methyl 7-oxo dehydroabietate (A), methyl 7 α -hydroxydehydro-abietate (B), 7 α -hydroxy-8 α ,9 α ,13 α ,14 α -diepoxide (C), cyclopropyl peroxide (D) and methyl 13 α ,14 α -epoxy-7 α -dihydroabietate (E). A, B and C were thought to be formed via the intermediate 7 α -hydroperoxypalustrate (F).

FIGURE A3.5: AUTOXIDATION OF METHYL ABIETATE BY SUNLIGHT.



(All the reactions in Figure II use O₂ and hv)