

Harpur Hill, Buxton
Derbyshire, SK17 9JN
T: +44 (0)1298 218000
F: +44 (0)1298 218590
W: www.hsl.gov.uk



Measurement of Hydroquinone

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Author: **Emma Scobbie**

Science Group: **Environmental Measurement**

SUMMARY

OBJECTIVES

The aim of this project was to investigate a method for the measurement of hydroquinone in air, in order to be able to demonstrate compliance with the proposed occupational exposure limit (OEL).

MAIN FINDINGS

As hydroquinone may occur in both the vapour and particulate phases, effective sampling requires a combination of a particle collector and a vapour collector. The sampler evaluated was a glass fibre filter contained in a multi-holed sampler which collects the particulate backed up with a tenax tube to collect any vapour. The samples were desorbed into acetonitrile and analysed by High Performance Liquid Chromatography (HPLC). This method was shown to be effective at measuring hydroquinone over the range 0.1 to 2 times the target exposure limit of 0.5 mg/m³ for 8 hours.

MAIN RECOMMENDATIONS

The following recommendations are made for sampling and analysis of airborne hydroquinone;

SAMPLING - Air samples are taken onto glass fibre filters with back-up tenax tubes at a flow rate of 2 l/min.

ANALYSIS - The filters and tenax tubes are immediately desorbed into acetonitrile and analysed by HPLC.

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1. INTRODUCTION

The main purpose of this work was to investigate methods for measuring personal exposure to hydroquinone and to demonstrate the adequacy of the developed method to cope with proposed occupational exposure limits. The target occupational exposure limit (OEL) was taken as 0.5 mg/m^3 (8 hour time weighted average, TWA).

Exposure to hydroquinone can cause skin irritation and sensitisation, and irritation to the eyes, nose and throat (HSC, 1995). Hydroquinone has also been shown to be mutagenic in animals and a no-adverse-effect-level cannot be identified in humans. Acute poisoning can cause dizziness, headache, unconsciousness, low temperature, tinnitus, breathing difficulties and a fast or feeble pulse. Hydroquinone is classified on the Approved Supply List (Chemicals (Hazard Information and Packaging) Regulations, 1994) as harmful and is labelled with risk phrases R20 and R22 : harmful by inhalation and if swallowed.

Hydroquinone is likely to occur in both the vapour and particulate phases in some atmospheres (Perez and Soderholm, 1991). It is subject to auto-oxidation in the presence of trace amounts of oxygen and can be oxidised easily in the presence of water vapour to form benzoquinone which is more volatile than hydroquinone. It is also oxidised when exposed to light.

Hydroquinone is used as a developer in black and white photography; an antioxidant for fats and oils; a polymerization inhibitor; a stabilizer in paints, varnishes, motor fuels, oils; an intermediate for rubber-processing chemicals; in the production of mono- and dialkyl-ethers; and as a depigmenting agent. In the photographic industry exposure to hydroquinone dust and solutions may occur during the manufacture of developers, and exposure to aerosols and mists containing hydroquinone may occur during bottle-filling. In other industries hydroquinone dust in the air is the major source of potential exposure.

Although some methods to measure exposure to hydroquinone have been published in the literature they have not been used by HSE and have not been fully validated.

2. OVERVIEW OF THE PROJECT

A search of the literature indicated several possible methods for the measurement of hydroquinone (Gattrell and Kirk, 1987; Huang et al, 1984; Levin, 1988; NIOSH, 1984; Risner, 1990; Risner and Cash, 1990). Hydroquinone may occur in both the vapour and particulate phases in some atmospheres (Perez and Soderholm, 1991) and the possibility also exists for oxidation to benzoquinone, present in vapour form. MDHS 14/2 (HSE, 1997) recommends personal samplers for total inhalable dust. Only one of the methods found in the literature (Levin, 1988) involves sampling for both vapour and particulate, but does not use a sampler recommended in MDHS 14/2 or distinguish between hydroquinone and benzoquinone.

The multi-orifice sampler recommended in MDHS 14/2 was used in this study, containing a glass fibre filter at a flow rate of 2 l/min. A back-up adsorbent tube was used behind the filter head to collect any hydroquinone or benzoquinone which may be present in the vapour phase.

Analysis was carried out by High Performance Liquid Chromatography (HPLC).

3. EVALUATION PROCEDURE

The performance of the samplers was tested under a range of conditions using the European testing protocol BS EN 482 for guidance.

4. ANALYTICAL METHOD

Samples were collected at 2 l/min onto glass fibre filters contained in multi-orifice heads according to MDHS 14 (HSE, 1997) with back-up tubes containing Tenax (50/100mg, dimensions 8x100mm). The samples were desorbed into acetonitrile (3ml) and analysed by HPLC using a Zorbax CN column (25cm x 4.6mm i.d.). The flow rate through the column was 1.5 ml/min. Hydroquinone was measured at 290 nm and benzoquinone at 245 nm. The spectra are shown in Figure 1.

Choice of mobile phase

Acetonitrile : water

A 30:70 acetonitrile : water mobile phase was found to give effective separation of hydroquinone (2.8 mins) and benzoquinone (3.4 mins). However, conversion of hydroquinone to benzoquinone appeared to be taking place in the system. The extent of this conversion varied with the concentration of hydroquinone, the amount of conversion being greater in the lower concentration hydroquinone standards.

Acetonitrile : dilute sulphuric acid(0.02%)

The oxidation of hydroquinone to benzoquinone is sensitive to pH. The water in the mobile phase was replaced with 0.02% sulphuric acid (~pH 2), in order to lower the pH and prevent oxidation occurring.

When the hydroquinone standards were analysed using this mobile phase, no benzoquinone was detected. Similarly no hydroquinone was detected in benzoquinone standards. Therefore use of an acidic mobile phase prevents interconversion of hydroquinone to benzoquinone in the HPLC system. However, under these conditions the HPLC column was being used at the limit of its recommended pH range. As a consequence, the chromatography gradually deteriorated and poor peak shapes were observed.

Acetonitrile : phosphate

The dilute sulphuric acid was replaced with 0.01M sodium dihydrogen orthophosphate (~pH4). This mobile phase appeared to prevent interconversion of hydroquinone and benzoquinone without adversely affecting the HPLC column.

5. MEASUREMENT RANGE

The current exposure limit for hydroquinone is 2 mg/m³ although in future it is likely to be set at 0.5 mg/m³ (over 8 hours). The target OEL for this work was therefore taken as 0.5 mg/m³. A suitable analytical method must be able to measure 0.1 to 2 times the exposure limit to satisfy the requirements of the CEN protocol.

A sample taken at 2 l/min for 8 hours (960 l) at 0.5 mg/m³ is equivalent to a collected mass of 0.48 mg. The analytical method must therefore be able to measure 0.048 - 0.96 mg per sample. If the samples are desorbed into 3 ml of acetonitrile then this range is equivalent to 0.016 - 0.32 mg/ml (or 160 - 3200 ng per injection of 10 µl). A linear response was observed for hydroquinone in this range.

Limits of detection and quantification are detailed in Appendix 1.

6. EVALUATION OF METHOD FOR HYDROQUINONE

6.1 Determination of desorption efficiency

6.1.1 Experimental

The desorption efficiencies of the filters and Tenax tubes were tested at 3 different levels by spiking with hydroquinone (a 10 µl solution in acetonitrile) and desorbing into acetonitrile (3 ml). An equivalent amount of hydroquinone was added to 3 ml acetonitrile for comparison. Similarly, the desorption efficiency of benzoquinone from Tenax was also tested at low levels.

The desorption efficiency was calculated as (the mass found on filter or tube / mass found in solution) x 100.

6.1.2 Results

The results are shown in Tables 1 to 3.

Table 1 : Desorption efficiency of GF/A filters

nominal concentration	mean ng hydroquinone detected		% desorption efficiency
	in solution	on filter	
0.1 x OEL	153 ± 2% (n=3)	154 ± 1% (n=6)	101
1 x OEL	1749 ± 2% (n=3)	1761 ± 1% (n=6)	101
2 x OEL	3196 ± 1% (n=3)	3256 ± 1% (n=6)	102

Table 2 : Desorption efficiency of Tenax tubes (hydroquinone)

nominal concentration	mean ng hydroquinone detected		% desorption efficiency
	in solution	on Tenax	
0.1 x OEL	145 ± 1% (n=6)	142 ± 2% (n=6)	98
1 x OEL	1619 ± 1% (n=6)	1585 ± 1% (n=6)	98
2 x OEL	3111 ± 2% (n=6)	3017 ± 2% (n=6)	97

Table 3 : Desorption efficiency of Tenax tubes (benzoquinone)

nominal concentration	mean ng benzoquinone detected		% desorption efficiency
	in solution	on Tenax	
20 ng	18 ± 1% (n=6)	16 ± 13% (n=6)	88
160 ng	166 ± 1% (n=6)	139 ± 11% (n=6)	84

6.1.3 Conclusions

Acetonitrile may be used to effectively desorb hydroquinone from both GF/A filters and Tenax tubes. Benzoquinone is desorbed from Tenax with an efficiency of around 84 to 88%.

6.2 The effect of temperature, humidity and concentration - preliminary study

These tests were designed as a preliminary study on the effect of temperature, relative humidity and concentration on the desorption efficiency. The aim was to use the results to help plan which further experiments would be necessary to fully understand the effects of temperature, humidity and concentration.

6.2.1 Experimental

A solution of hydroquinone in acetonitrile (10µl) was spiked onto glass fibre filters to give nominal concentrations equivalent to sampling an atmosphere of;

a) 0.5 mg/m³ for 8 hours at 2 l/min = 0.48 mg on the filter (1xOEL)

b) 0.05 mg/m^3 for 8 hours at 2 l/min = 0.048 mg on the filter (0.1xOEL)

The filters were desorbed into 3 ml acetonitrile and then 10 μ l injected into the HPLC for analysis, to give nominal concentrations of;

a) 0.16 mg/ml = 1600 ng/injection

b) 0.016 mg/ml = 160 ng/injection

Preliminary experiments were carried out at each concentration under three different combinations of temperature and relative humidity. For each set of conditions 12 filters were spiked. Six were placed into tins (controls) and six put into 7-hole head samplers. Three of the 7-hole heads were backed up with Tenax tubes. The flow rates were set at 2 l/min and the samplers placed in a standard atmosphere of air adjusted to the required conditions of temperature and humidity. Air was drawn through the samplers for approximately 6 hours. The filters and Tenax tube sections were each desorbed into 3 ml acetonitrile and analysed by HPLC.

6.2.2 Results

The results are shown in Table 4. At concentrations equivalent to 1 x OEL good recoveries of hydroquinone from the filter were found at temperatures of 20 and 30°C and humidities of 0 and 80% RH. Some hydroquinone was found on the back-up Tenax tube, typically 1 or 2% . A small amount of benzoquinone was also found on the Tenax tubes, typically 1 or 2% of total hydroquinone added (benzoquinone figures not tabulated).

At concentrations equivalent to 0.1 x OEL recoveries of hydroquinone from the filter were poor, between about 20 and 70%, depending on the conditions of temperature and relative humidity. An increase in temperature from 20 to 30°C appeared to cause a marked decrease in recovery. An increase in relative humidity between 0 and 80% RH may cause a slight decrease in recovery although the results are not conclusive. The hydroquinone lost from the filter appears to be trapped on the back-up Tenax tube. The recovery of hydroquinone from the filter + back-up was between about 80 and 90%. Some benzoquinone was also detected on the back-up tubes, between 2 and 6%.

Table 4 : Effect of temperature, humidity and concentration

conditions			mean hydroquinone on filter ng/injection (n=6)		mean hydroquinone on Tenax ng/injection (n=3)		total HQ ng/injection	recovery from filter %	total recovery %
concn.	temp.	humidity	controls	samples	front	back			
1xOEL	20°C	dry	1450	1419	32	0	1451	98	100
1xOEL	20°C	80%RH	1530	1365	16	0	1381	89	90
1xOEL	30°C	80%RH	1297	1201	70	0	1271	93	98
0.1xOEL	20°C	40%RH	158	107	29	0	136	68	86
0.1xOEL	30°C	dry	163	50	75	8	133	31	82
0.1xOEL	30°C	80%RH	146	30	94	4	118	21	81

6.2.3 Conclusions

Good recovery of hydroquinone was obtained from filters spiked at 1xOEL regardless of conditions of temperature and humidity. However poor recovery was obtained from filters spiked at 0.1xOEL.

The hydroquinone lost from the filters was found mainly as hydroquinone on the back-up tubes. A small percentage of benzoquinone was found on the back-up tubes.

Further experiments are required to clarify the results obtained, especially at low concentrations of hydroquinone.

6.3 The effect of temperature, humidity and concentration - further experiments

6.3.1 Experimental

In order to clarify the results obtained at low hydroquinone concentrations (Section 6.2) a further more extensive series of experiments was carried out at the 0.1xOEL level under the following conditions;

10°C, 20%RH and 70%RH; 20°C, 20%RH and 70%RH; 30°C, 20%RH and 70%RH

Experiments were also carried out at 1x and 2x OEL at the extremes of temperature and humidity in order to confirm the findings of the preliminary tests.

For each set of conditions 12 filters were spiked. Six were placed into tins (controls) and six put into 7-hole head samplers. Each of the 7-hole heads were backed up with Tenax tubes. The flow rates were set at 2 l/min and air was drawn through the samplers for approximately 6 hours at the required conditions of temperature and humidity. The filters and Tenax tube sections were each desorbed into 3 ml acetonitrile and analysed by HPLC.

6.3.2 Results

The results are shown in Table 5. At 0.1 x OEL the results show good recovery of hydroquinone from the filter at 10°C regardless of humidity. Approximately 3 or 4 % of the hydroquinone was found on the Tenax. At 20°C, about 70% of the hydroquinone was recovered from the filter at both 20%RH and 70%RH. Another 20% was found on the Tenax, giving a good total recovery. At 30°C poor recovery of hydroquinone was obtained from the filter and about 70 to 80% found on the Tenax. The total recovery was over 90% at the low humidity but only about 80% at the high humidity.

At 1 x OEL and 2 x OEL good recoveries were obtained at the extremes of temperature and high relative humidity.

Table 5 : Effect of temperature, humidity and concentration

conditions	mean hydroquinone on filter ng/injection (n=6)		mean hydroquinone on Tenax ng/injection (n=6)		total HQ ng/injection	recovery from filter %	total recovery %
	controls	samples	front	back			
	0.1xOEL, 10°C, 20%RH	133	125	7			
0.1xOEL, 10°C, 70%RH	154	143	5	0	148	93	96
0.1xOEL, 20°C, 20%RH	154	101	43	0	144	66	93
0.1xOEL, 20°C, 70%RH	159	112	30	0	142	70	89
0.1xOEL, 30°C, 20%RH	160	31	109	6	146	19	91
0.1xOEL, 30°C, 70%RH	167	21	104	6	131	13	79
1xOEL, 10°C, 70%RH	1761	1758	5	0	1763	100	100
1xOEL, 30°C, 70%RH	1711	1358	294	16	1652	79	97
2xOEL, 10°C, 70%RH	3256	3277	5	0	3282	101	101
2xOEL, 30°C, 70%RH	3365	3081	245	10	3336	92	99

6.3.3 Conclusions

At low hydroquinone concentrations temperature appears to have a significant effect on the recovery from the filter. Less is recovered at high temperature and more passes through onto the Tenax tube. The total recovery from the filter and back-up tube is good (90%+) under most conditions of temperature and humidity. At the extreme of high temperature and high humidity the total recovery falls to about 80%.

At higher concentrations of hydroquinone the effects of temperature and humidity are less marked.

6.4 Storage

This test is intended to establish how long samplers which have been exposed to hydroquinone may be stored before analysis. BS EN 482 requires that the mean values for the 2 sets of results corresponding to 0 and 14 days storage should not differ by more than 10%.

6.4.1 Experimental

Filters

Eighteen GF/A filters were spiked with 10 μ l of a hydroquinone solution in acetonitrile. The filters were then stored at room temperature in tins for up to 28 days in batches of 3, before being desorbed into acetonitrile (3 ml) and analysed. This was carried out at 2 levels of hydroquinone; 0.48 mg per sample (equivalent to 0.5 mg/m³ at 2 l/min for 8 hours, 1 x OEL) and 0.048 mg per sample (equivalent to 0.05 mg/m³ at 2 l/min for 8 hours, 0.1 x OEL).

Desorbed filters

Eighteen GF/A filters were spiked with 10 μ l of a hydroquinone solution in acetonitrile. The filters were desorbed immediately into acetonitrile (3 ml) and these solutions stored at room temperature for periods of up to about a month before being analysed. This was carried out at 2 levels of hydroquinone; 0.48 mg per sample (equivalent to 0.5 mg/m³ at 2 l/min for 8 hours) and 0.048 mg per sample (equivalent to 0.05 mg/m³ at 2 l/min for 8 hours).

Tenax tubes

Eighteen Tenax tubes were spiked with 10 μ l of a hydroquinone solution in acetonitrile at a hydroquinone concentration of 0.048 mg per sample (equivalent to 0.05 mg/m³ at 2 l/min for 8 hours). The tubes were capped and stored at room temperature in batches of 3 in plastic bags for up to a month. The tubes were then desorbed into acetonitrile (3 ml) and analysed.

6.4.2 Results

Filters

The results in Table 6 show that for filters spiked with a concentration around the OEL there is a 5% difference between the samples stored for 0 and 14 days, and a 10% difference between the samples stored for 0 and 28 days. However, for filters spiked with lower levels of hydroquinone (equivalent to 0.05mg/m³ over 8 hours) a quarter of the hydroquinone spiked onto the filter is lost over 14 days and almost half is lost over approximately 1 month.

Desorbed filters

The results in Table 7 show that once the filters are desorbed into acetonitrile, there is little loss of hydroquinone over a month.

Tenax tubes

The results (Table 8) show that for Tenax tubes spiked with a concentration equivalent to exposure at around 0.1 x OEL over 8 hours there is little loss of hydroquinone over 14 days (5% loss). However, a quarter of the hydroquinone is lost over 28 days. Table 8 shows that this observed loss of hydroquinone appears to be due to conversion of hydroquinone to benzoquinone. If benzoquinone levels are accounted for then the increasing losses of hydroquinone with time are compensated for by increasing levels of benzoquinone found.

Table 6 : The effect of storage on filters spiked with hydroquinone

storage time (days)	ng hydroquinone found	stored / fresh (%)
a) ~ 1 x OEL		
0	1573 ± 0.3%	---
1	1500 ± 0.7%	95
7	1573 ± 1.7%	100
14	1500 ± 0.5%	95
21	1446 ± 1.2%	92
28	1413 ± 3.6%	90
b) ~ 0.1 x OEL		
0	163 ± 0.5%	---
2	155 ± 0.4%	95
7	134 ± 2.3%	82
14	123 ± 5.9%	75
19	113 ± 4.1%	69
33	93 ± 7.8%	57

Table 7 : The effect of storage on desorbed filters (~ 0.1 x OEL)

storage time (days)	ng hydroquinone found	stored / fresh (%)
0	152 ± 0.4%	---
1	152 ± 0.4%	100
7	152 ± 1.1%	100
14	153 ± 2.1%	101
21	151 ± 2.0%	99
33	150 ± 1.9%	99

Table 8 : The effect of storage on Tenax tubes spiked with hydroquinone (~ 0.1 x OEL)

storage time (days)	ng found		stored / fresh (%)	
	hydroquinone	hydroquinone + benzoquinone	hydroquinone	hydroquinone + benzoquinone
0	153 ± 2.9%	---	---	---
1	141 ± 4.8%	143 ± 8.0%	92	93
7	142 ± 2.3%	149 ± 3.6%	93	97
14	145 ± 0.9%	151 ± 2.6%	95	99
21	120 ± 13.0%	143 ± 11.8%	78	93
28	114 ± 31.9%	154 ± 1.1%	75	101

6.4.3 Conclusions

The ability to store filters which have been exposed to hydroquinone depends on the amount of hydroquinone collected. Filters with hydroquinone levels equivalent to exposure at the OEL over 8 hours may be stored at room temperature for up to a month. However significant losses occur when filters with lower amounts of hydroquinone are stored. Some conversion of hydroquinone to benzoquinone occurs when Tenax tubes exposed to hydroquinone are stored. Therefore it is not appropriate to store filters or Tenax tubes which have been used to sample hydroquinone.

Exposed filters and Tenax tubes should be desorbed into acetonitrile as soon as possible after sampling. The solutions may then be stored for a month.

7. OVERALL UNCERTAINTY

The overall uncertainty for a measuring procedure is defined in BS EN 482 (British Standards Institution, 1994) as "the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure", and is quoted as a percentage combining bias and precision using the following equation:-

$$\text{Overall Uncertainty} = \frac{|\bar{x} - x_{\text{ref}}| + 2s}{x_{\text{ref}}} \times 100$$

where :

\bar{x} is the mean value of results of a number n of repeated measurements;

x_{ref} is the true or accepted reference value of concentration;

s is the standard deviation of measurements

An additional 5% is usually included to allow for the variability of the pump flow rate. The performance requirements quoted in BS EN 482 for overall uncertainty are $\pm 50\%$ for samples in the range 0.1 to 0.5 LV and $\pm 30\%$ for samples in the range 0.5 to 2.0 LV (LV = Limit Value).

The overall uncertainty of the method was determined to be less than $\pm 14\%$ for samples in the range 0.1 to 0.5 LV and less than $\pm 11\%$ for samples in the range 0.5 to 2.0 LV, i.e. well within the EN 482 specifications.

8. FIELD TRIALS

The primary aim of the field trials was to study the effect of any interferences which may be present in the workplace. Samples were taken at two locations where exposure to hydroquinone in the air may occur, either in the vapour phase (Field Trial 1) or as particulate (Field Trial 2).

8.1 Field Trial 1

This field trial was carried out in two separate hospital X-Ray Processing departments where hydroquinone was a constituent of the X-Ray film developers used. In each department there were two automatic X-Ray film processors which were in constant use throughout the day. The processing occurs at a temperature raised above ambient, approximately 30°C, and it was thought that hydroquinone may be present in the air in its vapour form. Six samplers were placed on top of a processor in each department and samples were taken over 6 hours at 2 l/min. The samples were desorbed into acetonitrile on the day after sampling.

The levels of hydroquinone were below the detection limit (i.e. $< 0.4 \mu\text{g}/\text{m}^3$). Also no benzoquinone was found. No interference was observed from other species which may be present in the air in such areas, such as volatile components of the developer or fixer solutions.

8.2 Field Trial 2

This field trial was carried out at a site where film developers are produced. Samples were taken during the addition of bulk hydroquinone to the mixing vessel. During this procedure, which takes approximately 40 minutes, the operator cuts open 25kg bags of hydroquinone

and empties their contents into the mixer. The mixer is under extraction throughout. Six samplers were placed on top of the mixer (samples 1 to 6) and six were placed by the side of the mixer at ground level (samples 7 to 12). A further sampler was attached to the lapel of the operator (sample 13).

Samples 1 to 6 were below the detection limit (i.e. $< 2 \mu\text{g}/\text{m}^3$). The results for samples 7 to 13 are shown in Table 9. Example chromatograms are shown in Figures 2 and 3.

Table 9 : Results of Field Trial 2

sampler	sample volume l	μg detected on sampler			$\mu\text{g}/\text{m}^3$	
		hydroquinone*	benzoquinone [#]	total	hydroquinone	total
7	100	0.57	1.98	2.55	5.7	25.5
8	100	0.90	1.71	2.61	9.0	26.1
9	100	0.81	1.89	2.70	8.1	27.0
10	100	0.75	1.77	2.52	7.5	25.2
11	100	0.63	1.50	2.13	6.3	21.3
12	100	-	1.26	1.26	-	12.6
13 (personal sample)	90	1.83	2.46	4.29	18.3	47.7

* found on filter section; # found on Tenax back-up section

The results for samples 7 to 12 (Table 9) show that very low levels of hydroquinone and benzoquinone were detected in the static samples. The hydroquinone was all found on the filter section, whereas all of the benzoquinone was found on the adsorbent back-up. There is good agreement between samplers 7 to 11. Sampler 12 appears to be an outlier.

Slightly higher levels were detected on sampler 13 which was worn by the worker whose job was to add the bulk hydroquinone to the vessel. This would be expected as this sampler was closest to the procedure involving the hydroquinone.

No interferences were caused by other species present in the workplace atmosphere. The main possible interferent in this situation would be potassium carbonate which is added to the mixing vessel immediately after the hydroquinone.

9. DISCUSSION AND CONCLUSIONS

Pumped sampling onto glass fibre filters with back-up Tenax tubes offers an effective means of monitoring hydroquinone. The method appears to have sufficient sensitivity to cover the range 0.1 to 2 times the target exposure limit of $0.5 \text{ mg}/\text{m}^3$ for 8 hours.

The desorption efficiency of hydroquinone from GF/A filters and Tenax tubes was shown to be effectively 100%. For most conditions of temperature and humidity the recovery of hydroquinone (from combined filter and back-up) is good (>90%). However lower recoveries are seen (~80%) at the extremes of high temperature and humidity. The distribution of the hydroquinone between the filter and back-up depends on temperature.

Losses of hydroquinone may occur from exposed filters and therefore filters should be desorbed into acetonitrile as soon as possible after sampling. These solutions can then be stored for up to a month.

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APPENDIX 1

DETECTION AND QUANTIFICATION LIMITS

The limit of detection (LOD) gives an indication of the smallest amount of hydroquinone in a sample which may be positively identified. It is defined as the concentration which gives a signal to noise ratio of 3 : 1.

The limit of quantification (LOQ) is defined as the smallest amount of hydroquinone which may be confidently quantified in a sample. It is defined as the concentration which gives a signal to noise ratio of 10 : 1.

Typical LOD and LOQ values observed during this work were :-

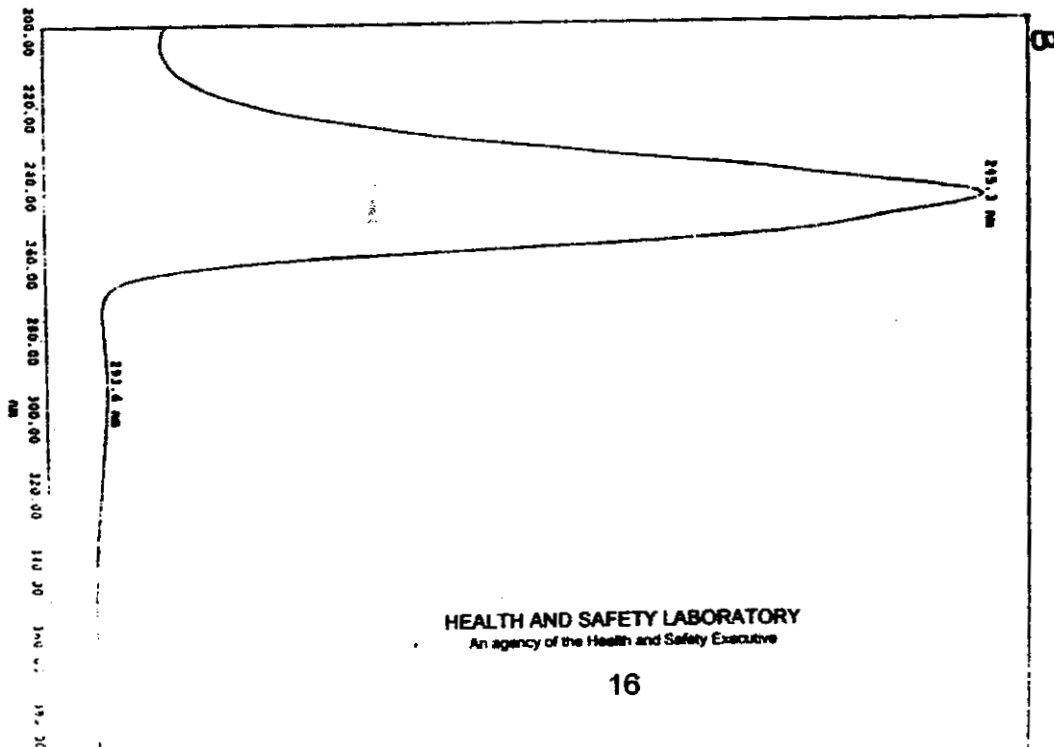
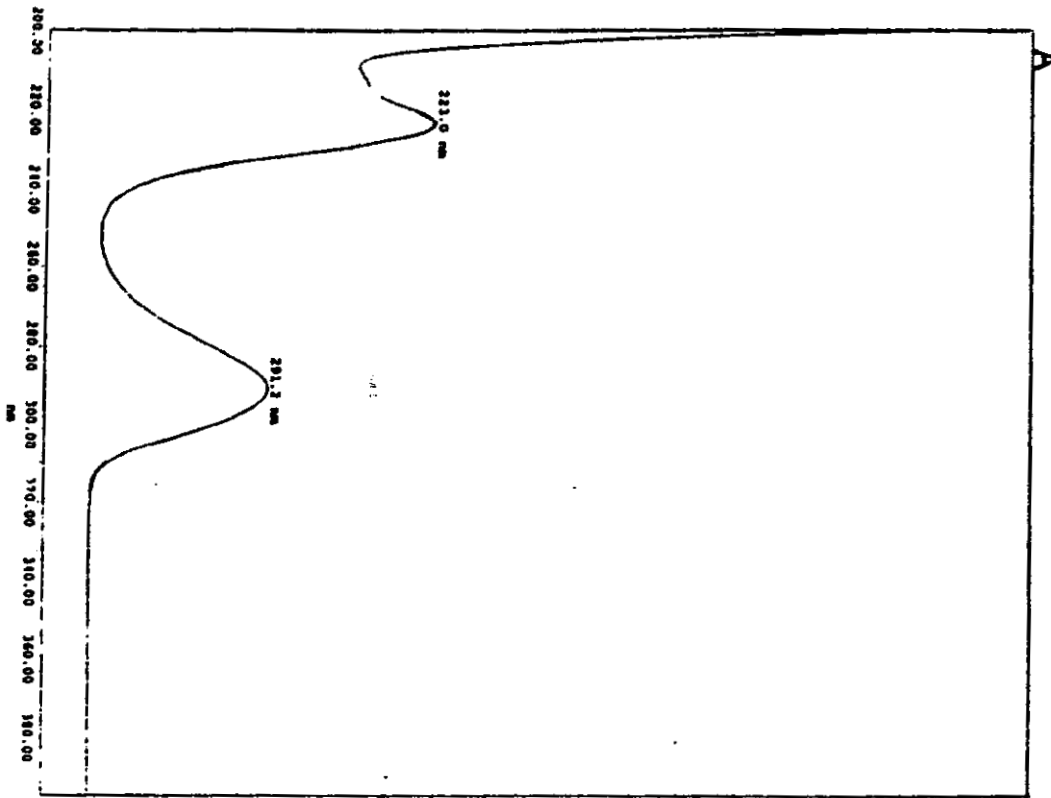
LOD = 1 ng per 10 μ l injection (= 0.3 μ g per sample when desorbed into 3 ml = 0.3 μ g/m³ for an 8 hour sample taken at 2 l/min)

LOQ = 4 ng per 10 μ l injection (= 1.2 μ g per sample when desorbed into 3 ml = 1.3 μ g/m³ for an 8 hour sample taken at 2 l/min)

Figure 1 : uv spectra of hydroquinone and benzoquinone;

A hydroquinone

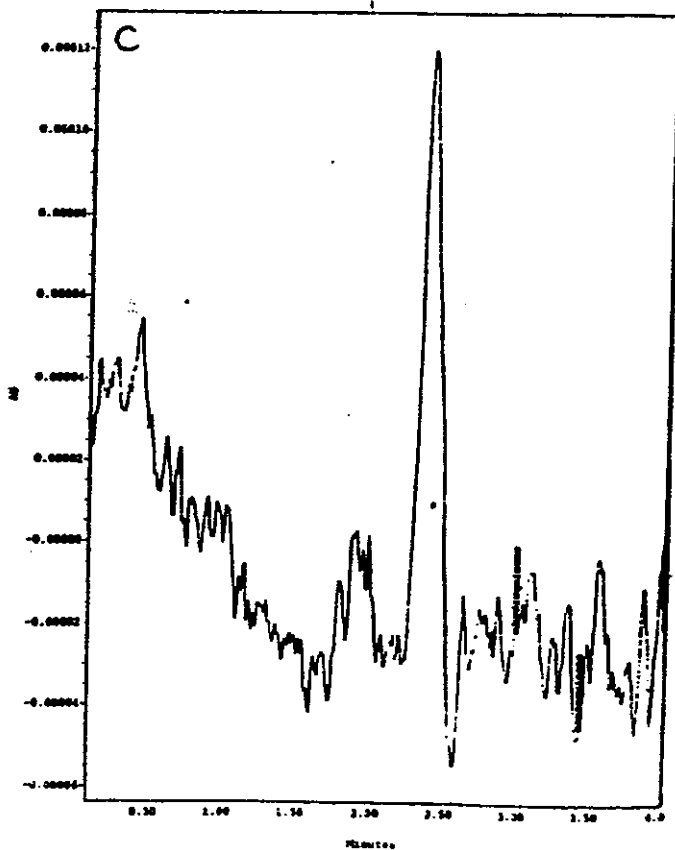
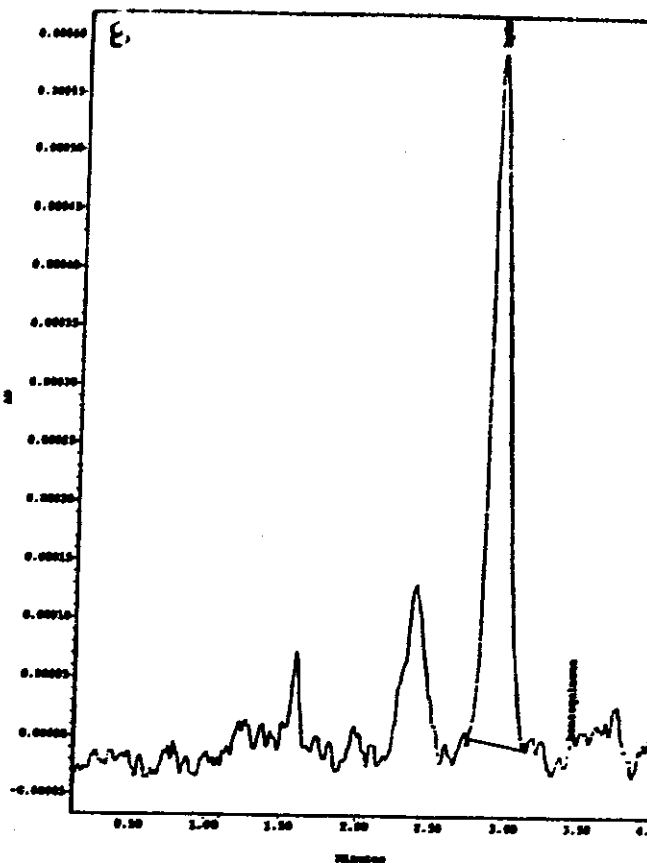
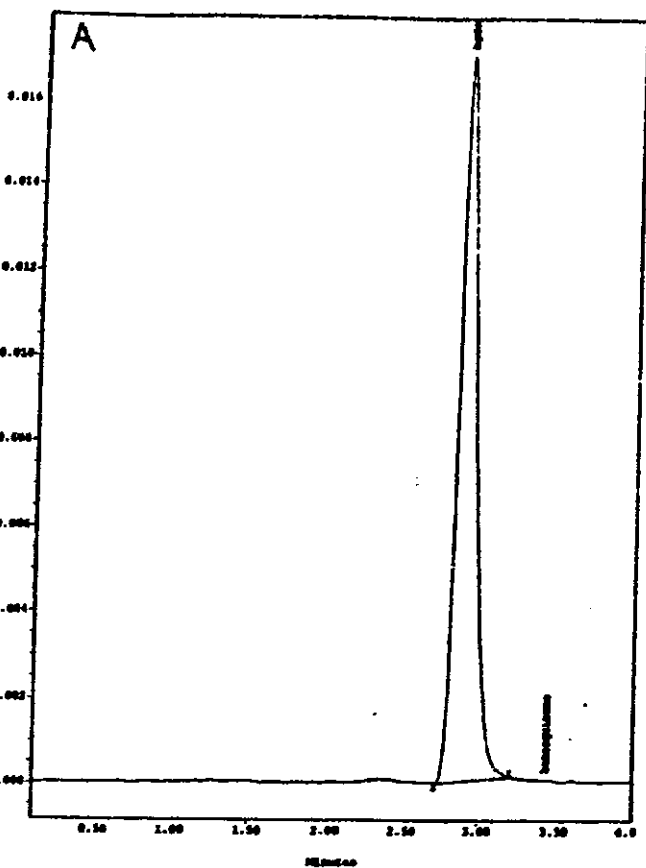
B benzoquinone



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Figure 2 : HPLC trace for hydroquinone;

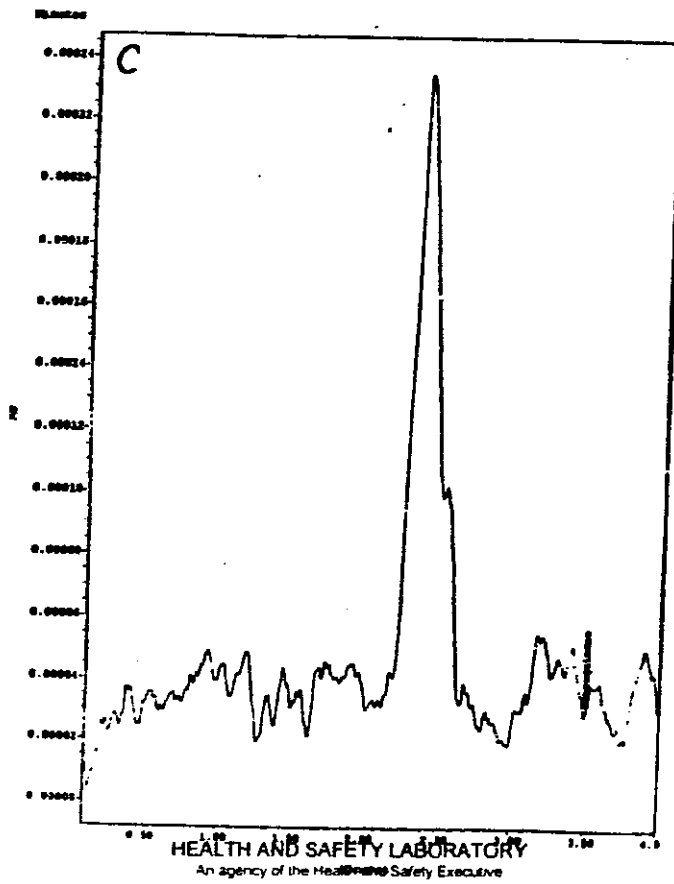
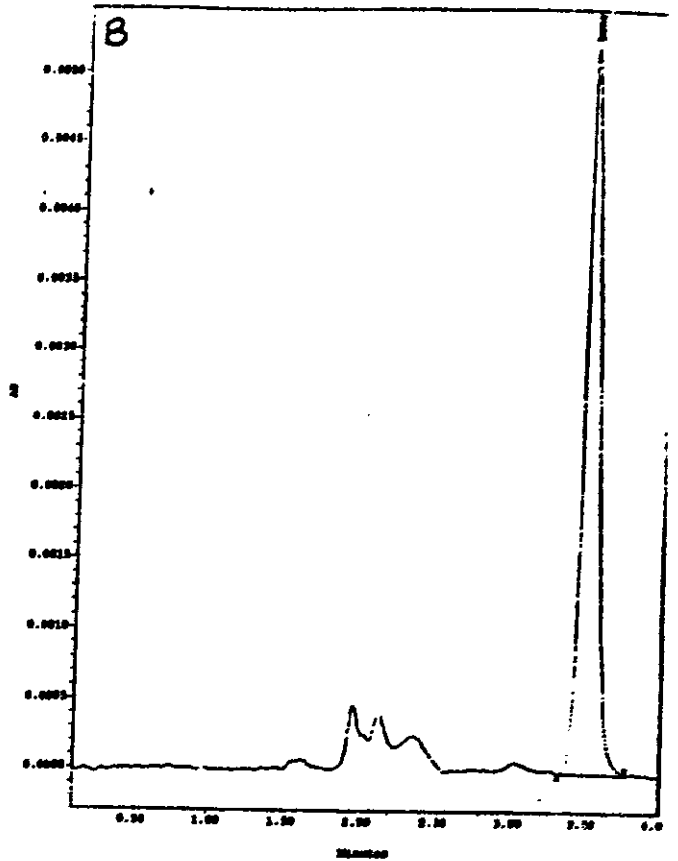
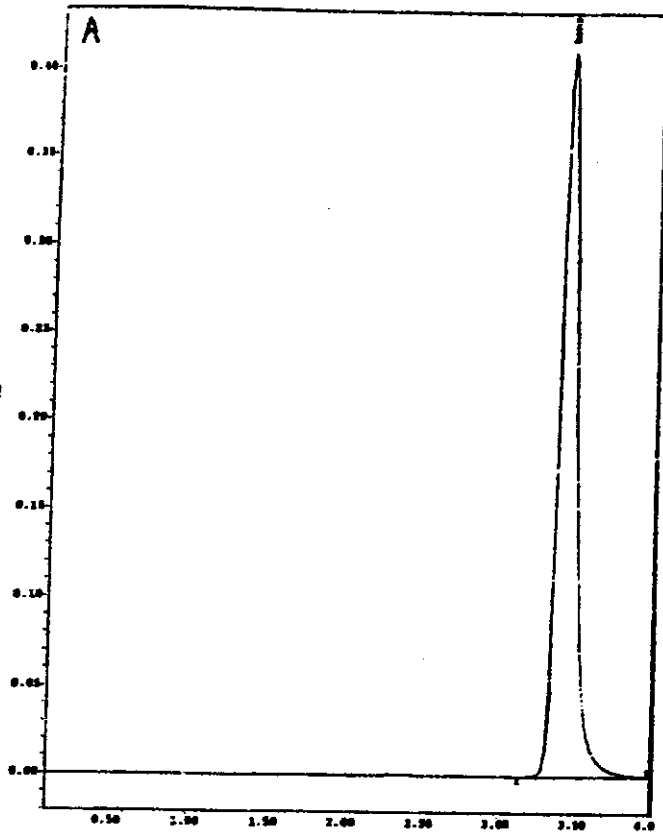
A standard; B sample; C blank



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Figure 3 : HPLC trace for benzoquinone;

A standard; B sample; C blank



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