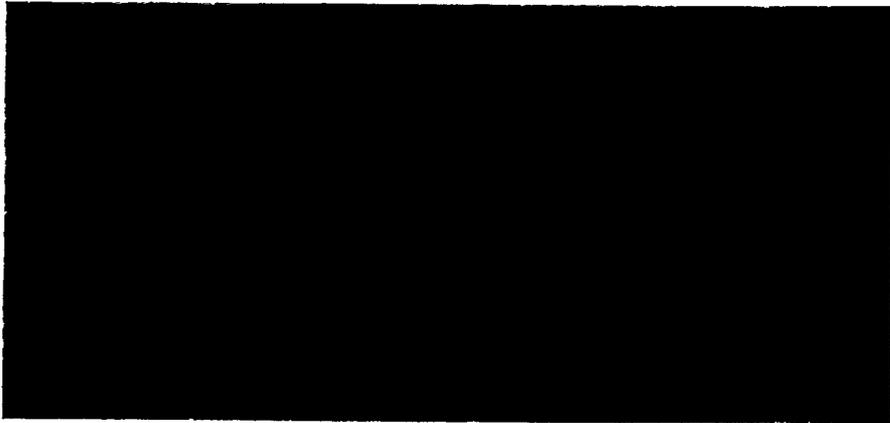


WATER RESEARCH

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COAL-TAR PITCH PARTICLES IN DRINKING WATER

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SUMMARY

The objective of the work outlined in this report was to determine the extent to which drinking water supplies are contaminated with particles of coal-tar pitch derived from pipe linings. The work carried out stemmed from a WRC survey of polycyclic aromatic hydrocarbon levels in British waters in which the possibility emerged that drinking water may be contaminated with particles of coal-tar pitch arising from the linings of iron distribution pipes.

In Great Britain about 60% by length of the distribution pipes laid for the Water Industry are of ductile iron and the majority of these have been coated internally with coal-tar pitch according to BS 4164. Since 1978 there has been no further use of coal-tar pitch for this purpose.

Such linings, and any derived particles, can contain up to 50% polycyclic aromatic hydrocarbons (PAH), some of which (eg benzo[a]pyrene) are carcinogenic.

The subject was discussed with appropriate bodies in late 1975 and there was general concern about the possibility of particles of lining material, containing substantial proportions of carcinogens, lodging in the digestive tract. It was decided that information was needed on the exposure of people to such particles.

The result was that a contract was placed by the Department of the Environment with WRC for studies on the occurrence of coal-tar pitch particles in drinking water. This work was reported to the Department in 1983.

The experimental approach adopted was to examine mains deposits and particles collected from tapwater. Attempts were made to develop methods designed to characterise (size, number, chemical composition) individual particles. One such method showed promise (laser microprobe mass analyser) but would require considerable effort and expense to produce a routine method suitable for use in a survey. As a back-up technique particles were extracted with an organic solvent and the extracts analysed by gas chromatography for the presence of PAH indicative of coal-tar pitch.

Due to the time needed to develop and test suitable techniques and the slowness of the methods that emerged, a wide survey of drinking waters was not feasible. However, in the limited number of tapwaters examined one sample exhibited high levels of coal-tar pitch. To obtain information on detailed exposure to coal-tar pitch particles via tapwater, on a large scale, will be technically very difficult and extremely expensive.

Mains deposits frequently contained relatively massive levels of PAH due to the presence of coal-tar pitch particles. Coal-tar pitch particles down to at least 3 μm diameter were detected in these deposits and one would expect such particles to be 'mobile'. Any situation that disturbs the deposits, such as mains renovations and flow reversals, could release coal-tar pitch particles in the water. Such situations need to be examined.

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1. INTRODUCTION

The objective of the work outlined in this report was to determine the extent to which drinking water supplies are contaminated with particles of coal-tar pitch derived from pipe linings. The work stemmed from a survey of polycyclic aromatic hydrocarbon levels in British waters (Crane et al 1981) in which the possibility emerged that drinking water may be contaminated with particles of coal-tar pitch arising from the linings of iron distribution pipes.

In Great Britain about 60% by length of the distribution pipes laid for the Water Industry are of ductile iron and the majority of these have been coated internally with coal-tar pitch according to BS 4164. Since about 1977 there has been no further use of coal-tar pitch for this purpose. Typically, lining was performed by immersing the pipe section in a bath of coal-tar preparation held at high temperature. BS 4164 specifies types I to IV coal-tar preparations, but types I and III (containing no filler) were the commonly applied materials. Type I was a straight coal-tar pitch while type III was a modified pitch produced by the hot digestion of a small quantity of coal dust in anthracene oil. (Anthracene oil is a high-boiling coal-tar fraction, resembling pitch but with a lower viscosity.) In recent years type III was used in the larger quantity.

Such linings, and any derived particles, can contain up to 50% polycyclic aromatic hydrocarbons (PAH), some of which (eg benzo[a]pyrene) are carcinogenic. While actual amounts of PAH consumed as particles (in terms of PAH concentration in drinking water) may be very small, the proportion of PAH in each particle would be exceedingly high.

The matter was discussed with various bodies in late 1975 and there was general concern about the possibility of particles of lining material, containing substantial proportions of carcinogens, lodging in the digestive tract and decided that information was needed on the exposure of people to such particles.

The result was that a contract was placed by the Department of the Environment with the Water Research Centre (WRC) for studies on the occurrence of coal-tar pitch particles in drinking water. This contract ended in 1983.

This report summarises the experimental approach and the findings and makes some recommendations. Experimental detail is covered by several appendices.

2. EXPERIMENTAL

2.1

General considerations

At the start of the work there seemed to be a number of questions requiring consideration:

- a) What is the size range of particles of interest?
- b) Where to take samples?
- c) What methods are needed to collect particles from water?
- d) How can particles be counted, sized and identified?

A literature survey revealed that no general experience of studying particles in water existed. One piece of work referred to counting particles

before and after water treatment processes, as an alternative control method to turbidity measurements (Tate and Trussell 1978). No information was found on the types of particles in drinking water.

Having received no information from medical experts on the size range of particles likely to be trapped and absorbed by the digestive tract, it was decided to work in the size range 1 micron ($1\ \mu\text{m}$, 10^{-6} metre) and larger, this being the range of optical microscopy. To work with particles smaller than this, almost inevitably, involves electron microscopy. But, generally, organic material is destroyed in the preparation of samples for electron microscopy, thus removing any chance of chemically identifying organic species, such as coal-tar pitch, in the final sample preparation.

It was realised that no ready-made set of techniques existed for solving the whole problem. Two approaches were adopted to obtain samples on which to work. First, large quantities of mains deposits were collected, giving ample material for development of techniques. It was reasoned that if particles from coal-tar pitch linings are to be found anywhere in a distribution system then the most likely place to find them is in the sediment arising from corrosion of the iron under the linings. Also systems could be located which could be used for further study with techniques applicable to tapwater. Second, particles were collected from large volumes of drinking water. It proved time-consuming to collect and process such samples and the yields of particles were low.

Similarly, two different approaches were followed in trying to estimate the amount of coal-tar pitch particles in mains sediments and drinking water samples. The most desirable solution to the

problem would be a method or combination of techniques capable of counting, sizing and identifying individual coal-tar pitch particles. The possibility of technical problems could be foreseen and the successful development of an overall technique suitable for the 'routine' identification of individual coal-tar pitch particles could not be guaranteed. Therefore as a back-up method, samples of mains sediments and particles isolated from drinking water were extracted with an organic solvent and the extracts analysed by gas chromatography for the amounts of PAH present. This method gives estimates of the amounts of coal-tar pitch present in the particulate samples.

2.2

Sampling and samples

2.2.1

Mains deposits

Since tapwater contains relatively small amounts of suspended matter it was decided to collect deposits from water mains in order to have large amounts of particulate sample on which to test techniques.

At WRc there were two sets of samples (A1, A2 and A3, and B1, B2 and B3) obtained from mains flushing exercises in 1978. The samples had been collected at hydrants either in plankton nets (A1, A2 and B3) or by collecting the water passing through the nets (A3, B1 and B2) and allowing it to settle in a tank. Sample C was the material collected by a foam swab by a water utility in response to a consumer complaining of "black bits" in the water. The sample came to WRc originally in association with an enquiry arising from the consumer's complaint. It had been examined by infra-red spectroscopy and found to contain aromatic compounds which were probably PAH. Sample D arose from another enquiry relating to widespread particle contamination of a system of trunk mains.

A further three samples (E, F and G) were collected during air-scouring exercises in areas with different source water types but all with histories of discoloured water problems. Two further samples of deposits were collected by flushing at hydrants. The first of these (H) was on a distribution system where the lining had previously been observed by WRc personnel to be blistered but apparently without corrosion of the underlying iron pipe. The second (J) was from a system where the concentration of PAH in the tapwater was high and the ratio of PAHs (fluoranthene/pyrene) had been found to be unusual.

2.2.2

Drinking water samples

Particles are a minor constituent of drinking water and it is assumed that coal-tar pitch particles, if any, are a minor constituent of the particle fraction. Therefore, it seemed likely that large volumes of water would have to be processed in order to collect enough material for study.

Among possible ways of collecting particles from aqueous suspension are gravitational settling, filtering and centrifuging. Settling under natural gravity is slow; in theory a 1 μm spherical coal-tar pitch particle falls through still water at 0.15 mm hr^{-1} . Filters from which particles can be removed after the filtration process or studied in situ, ie surface filters as opposed to depth filters, have a very low sample capacity and block quickly. Continuous centrifuging was chosen for this work because it speeds up the particle collection process not only by increasing the settling rate of particles but also by having a large sample volume processing rate.

The continuous centrifuge (Appendix C) used operates at nearly $6000xg$ and could, if necessary, take a flowrate of up to 100 l hr^{-1} without

flooding the input and output channels. A theoretical treatment making worst-possible-case assumptions of the ability of the centrifuge to retain coal-tar pitch particles from water is given in Appendix C.1. The size of the smallest coal-tar pitch particle likely to be retained is related to the speed of the water flowing through the centrifuge bowl. Thus at a flowrate of 20 l hr^{-1} coal-tar pitch particles of $1 \text{ }\mu\text{m}$ diameter ought to be captured.

The performance of the centrifuge (Appendix C.2) was evaluated using aqueous suspensions of latex spheres of known size distribution and density. The latex spheres were dispersed in water and the particle size distribution measured using a Partoscope F (Appendix A.6). The dispersion was passed through the centrifuge at a known flowrate and the particle size distribution in the effluent measured. The experiment was repeated with three different sizes of latex spheres. The complete results are in Appendix C.2 but, for example, at 29.6 l hr^{-1} more than 90% of $3.0 \text{ }\mu\text{m}$ latex spheres (equivalent to $1.97 \text{ }\mu\text{m}$ diameter coal-tar pitch spheres) were retained.

At the end of a centrifuge run the bowl contains retained material as a suspension in water with a volume of about 400 ml. After an early run in the project the suspension was taken to the Occupational Medicine and Hygiene Laboratory (HSE) for further processing and examination of the captured particles by electron microscopy. It was discovered that particles down to $0.3 \text{ }\mu\text{m}$ diameter had been trapped, although these were metals or metal salts and therefore considerably denser than coal-tar pitch. These results indicate that the continuous centrifuge was an effective way of collecting particles from drinking water.

Unfortunately, the continuous centrifuge had two disadvantages. Early in the work it was realised that the centrifuge was too noisy and inconvenient to use in consumers' houses and that connected directly to a mains tap variations in mains pressure allowed the flowrate through the centrifuge bowl to fluctuate widely. Therefore samples (usually 1.2 m³) were collected in a bowser and returned to the laboratory for processing. The water was pumped from the bowser by nitrogen top pressure to a 20 l aspirator. The water in the aspirator was fed to the centrifuge through a short flexible tube fitted with an adjustable clamp, which allowed the flowrate to be controlled (Figure A.4, Appendix D).

Five samples (M, N, Q, P, R) were collected and processed by the techniques described above. Some samples (M, P, Q and R) were taken at sites where mains deposits had also been collected. Thus M corresponds to deposit J, P to deposit H, Q to deposit G and R to deposit F. Sample L was from the laboratory at Medmenham water supply. Sample K was also from the laboratory drinking water supply but consisted of particles collected over a long period of time (several months) by a nominal 10 µm in-line cartridge filter sited in the laboratory mains supply. The nature of the sources of the tapwaters sampled were as follows:

Sample	Original Source of Water	Comments
K	Chalk aquifer	
L	Chalk aquifer	
M	Chalk aquifer	Borehole; corresponds to sediment J
N	Chalk aquifer	Unconfined aquifer, overlain with gravel
P	Stored river water	Corresponds to sediment H
Q	Stored river water	Corresponds to sediment G
R	Upland catchment	Corresponds to sediment F

2.3

Characterisation of particles

Numerous methods of particle counting and sizing are well established. Of these Coulter (electric zone) and optical methods can give information about the number and size distribution of particles in suspension (Appendix A). Microscopy, with or without automatic image analysis (Appendix G), can be used to describe the number, size, shape and optical properties of suitably presented samples. Previous work (Crane et al 1981) on PAH, had relied on the intense fluorescence of these compounds for their detection and estimation. Consequently, it was thought that fluorescence microscopy with automatic image analysis might be a useful method for detecting coal-tar pitch particles in a matrix of other particles.

At present a rapid expansion in the range of techniques being applied to the chemical characterisation of surfaces and particles is taking place. Two of these techniques, LAMMA and MOLE, will be discussed later (Sections 2.3.3 and 2.3.2 respectively).

2.3.1

Fluorescence of particles

Many polycyclic aromatic hydrocarbons in solution are intensely fluorescent under ultra-violet illumination. Therefore, it was hoped that coal-tar pitch particles could be recognised in particles isolated from drinking water, by fluorescence of their constituent PAH - especially if the latter could be caused to migrate sufficiently to produce specific, detectable "halos". A fluorescent "map" of a sample could then be studied by image analysis techniques in order to produce a particle count and size distribution selective for coal-tar pitch.

Initially a trial experiment to observe fluorescence from solid coal-tar pitch particles was made by coating particles of polycarbonate

membrane using trigol (a viscous, high-boiling alcohol). The trigol was necessary to hold the particles because the membrane had to be mounted vertically in the sample chamber. The membrane was stuck with double-sided adhesive tape on a metal post in the beam of a spectrophotofluorimeter. Although the adhesive tape gave a large fluorescent background, an emission spectrum (excitation wavelength 310 nm) was obtained with peaks above background at 370, 405 and 435 nm which could arise from PAH.

Further experiments were made using fluorescence microscopes and various illumination conditions. Coal-tar pitch particles showed only localised fluorescence. (This seemed to be due to crystals of PAH on the surface of some coal-tar pitch particles.) Preparations of particles were treated with various solvents and solvent vapours in order to try to induce a more general fluorescence of the particle surfaces or a fluorescent "halo" around each particle. However the only result of these treatments was to induce general fluorescence of the background against which the coal-tar pitch particles and other particles appeared as black silhouettes.

Thus no suitable images were obtained that could allow coal-tar pitch particles to be discriminated by image analysis.

Samples were sent to Professor J S Ploem (University of Leiden) for examination by microspectrofluorimetry. Initial results were promising in that fluorescence emission from coal-tar pitch particles was observed. However, other fluorescent particles, possibly of algal origin, were also found in some samples and because fluorescence spectroscopy (at least under ambient temperatures) has inherently low spectral

resolution, there is always a strong possibility of interferences. It is believed that the spectra are of very localised areas of particles. The experiments described in the following section make it clear that coal-tar pitch is a very efficient absorber of light which it converts to heat rather than emitted fluorescence.

2.3.2

MOLE

MOLE is the Jobin-Yvon trade-name of a laser Raman spectrophotometer microprobe. A MOLE is operated by the University of Bradford on a contract basis. The apparatus gives Raman spectra (vibrational spectra extracted from scattered visible light) from samples down to 1 μm diameter. The excitation source is a laser giving green light which is focused on the sample with a microscope objective. The scattered light is collected and analysed in a spectrometer. The system can also be used to build up an image of the sample at a single Raman line.

The MOLE has been used to identify particles and "regions of particles". It has found uses in geology (identifying different crystals within a matrix) and the textile industry (identifying the impurities responsible for failures in yarn strength). It was hoped that the discriminating power of the instrument would allow the identification of coal-tar pitch in a matrix of other particles.

A good spectrum of fluoranthene was obtained from a pure crystal but coal-tar pitch samples melted in the light beam and did not scatter the exciting light. Being black, coal-tar pitch is a very efficient absorber of radiation which it converts to heat. (Coal-tar pitch is such a complex mixture of substances that there are many energy levels available which provide pathways for dissipating the absorbed light as heat.) Although some

possibilities exist for avoiding the problems encountered, such as cooling the samples, it was considered that the chances of success would be low.

2.3.3

LAMMA

LAMMA is the Leybold-Heraeus GmbH (Cologne) acronym for their laser microprobe mass analyser. In this technique a laser beam is focussed with a microscope objective onto a particle of interest, which is then vaporised and to some extent ionised in the process. The ions produced are collected by an electrostatic lens and analysed in a time-of-flight mass spectrometer. Thus, potentially, such a system could detect a coal-tar pitch particle by means of the ions generated which would be characteristic of PAH.

Some samples were analysed on a LAMMA 500 instrument. The detailed results are given in Appendix F but briefly the following important points emerged:

1. Coal-tar pitch is easy to recognise by the LAMMA technique.
2. Coal-tar pitch particles, down to 3 μm diameter, were found in two samples of mains deposits (C and E, Table 1).
3. Mixed particles of coal-tar pitch and iron were also observed in these samples.
4. No coal-tar pitch was found in the two samples of particles isolated from drinking water which were examined (K and L). Sample L contained particles of lead, tin and indium, possibly fragments of a bearing.

5. Particles of petroleum bitumen origin
(Sample D) showed no characteristic ions that could be used as a diagnostic test for bitumen.

For the present project the LAMMA 500 instrument has the drawback that it operates in the transmission mode which limits the thickness of samples that can be examined to less than 10 μm . The LAMMA 1000 machine has been introduced recently which uses reflection geometry, allowing the examination of the surfaces of larger samples.

For the purposes of screening a large number of particles some development work is needed. It should be possible, using a combination of existing technologies, to build an instrument embodying the LAMMA 1000 to provide for an automated examination of a large area of sample and output of a coal-tar pitch map of the sample by recognition in the data of ions characteristic of PAH.

2.4

Estimation of coal-tar pitch particles by PAH analysis

The amount of coal-tar pitch in particulate matter was estimated by determining the content of PAH. The coal-tar pitch used to line water mains invariably consists of about 50% PAH. Fluoranthene and pyrene are two of the predominant PAH present. Analysis of a recent unused lining by gas chromatography (GC) gave 5.4% by weight fluoranthene and 4.9% by weight of pyrene. Although broadly similar, coal-tar pitches do not all have exactly the same quantitative composition. Therefore, estimates of the amount of coal-tar pitch present in isolated particulate matter was determined assuming that coal-tar pitch contains 5% by weight of fluoranthene (and pyrene). This procedure gives a basis on which to estimate the amount of coal-tar pitch and to compare samples.

The PAH was extracted by dripping hot solvent (dichloromethane) through a weighed amount of sample held in a glass thimble fitted with a sintered glass frit bottom (Figure A.5, Appendix E). After extraction the solid samples were dried and weighed to determine the amount soluble. In the case of particulate matter recovered from tapwater the quantities were very small and consequently the solubilities determined are very approximate.

The extracts were analysed by capillary column gas chromatography and the concentration of fluoranthene and pyrene determined. Some extracts were also examined by gas chromatography-mass spectrometry (GC-MS) and field desorption-mass spectrometry (FD-MS) to confirm identities of PAH generally, of trace quantities of PAH and of unusual components. (Appendix E gives experimental details and Table A.3 gives detailed results.)

2.5

Stability of coal-tar pitch particles in water

Although small particles of coal-tar pitch might be formed and released from a lining, eg by damage caused by corrosion under the lining, it is possible that once released such particles could have a limited lifetime. For example, while the coal-tar pitch enamel itself is to all intents and purposes insoluble in water, a 1 μm diameter particle with a weight of 10^{-12} g may be soluble. Therefore, the stability of coal-tar pitch particles in water was investigated.

A suspension of coal-tar pitch particles was made in water containing a small quantity of non-ionic detergent to aid dispersion of the particles. Portions of the suspension were filtered onto various types of membrane filters. The filters were examined under a microscope and photographs taken of the particles. The photographs showed

that considerable agglomeration of the particles had occurred and that it was difficult to see any single particles. In addition under a variety of different illumination conditions there was insufficient contrast between particles and background for reliable image analysis (Appendix G).

Therefore, it was decided to follow size distribution changes with time using the particle counter (Appendix A.6). A sample (2000 ml) of low-particle-count water (Appendix B) was examined with the particle counter operating in a continuous cyclic mode. Each cycle of cleaning and sample counting was longer than normally employed. Sample was pumped from close to the bottom of the sample vessel and returned to the top of the vessel. This scheme of operation was thought to have a number of advantages:

- a) good sample mixing would be maintained
- b) a particle count would be large, ensuring good statistics
- c) the pump would be kept running ensuring consistent speed and successive sample volumes.

The results showed that there was a steady build-up in the particle count. The reason for this has not been established but it could arise by shearing of the large particles as they pass through the very small flow cell of the pump.

More work into the stability of coal-tar pitch particles in water is justified.

3. RESULTS AND DISCUSSION

3.1

Characterisation of coal-tar pitch particles

A reasonably sensitive method of characterising individual coal-tar pitch particles in the presence of an abundance of other types of particles was sought. Some attempts at characterisation were largely unsuccessful, the results as such are covered in Section 2.3 and, in the case of LAMMA, in Appendix F. As mentioned previously, it was hoped that a method could be developed based on image analysis on the fluorescence emitted by coal-tar pitch particles, especially by means of solvent-induced "halos" (see Section 2.3). However, this did not work. Of the other techniques studied that offered some potential for characterisation, only LAMMA showed promise. Coal-tar pitch particles down to about 3 μm were detected in two deposits (samples C and E). With further development of sample scanning and data handling an effective method could be developed. However, this would need more resources and utilise very expensive instrumentation.

Thus most of the information produced was based upon the indirect estimation of coal-tar pitch particles by PAH measurement.

3.2

Estimation of coal-tar pitch particles by analysis of PAH

3.2.1

Coal-tar pitch in deposits lying in water mains

The solubility of the deposits in dichloromethane (see Table 1) usually fell in the range 1.8 to 21% by weight. In this context it should be borne in mind that coal-tar pitch itself is about 50% soluble in dichloromethane. The very high

solubility for sample D (75%) seemed to be due to the presence of bitumen lining (of petroleum origin) rather than coal-tar pitch.

The chromatograms of extracts of mains deposits (except sample D) gave the characteristic PAH pattern of coal-tar pitch. Figure 1 shows the composition for sample C as an example. Close similarity to "pure" coal-tar pitch should be noted (see Figure 2). No other organic substances were normally detected by GC with the exception of dialkyl phthalate esters (probably of plasticizer origin). Sample D gave no GC peaks, which agrees with its supposed bitumen origin - such material is not normally amenable to GC. Samples A1, A2, A3, B1, B2, D, E, F and H were also examined by GC-MS to confirm the identity of peaks and confirm the findings generally.

Confirmatory evidence was also obtained by FD-MS for samples F, G and H. Sample F, in addition to the usual range of PAH, showed material of molecular weight 302 and formula (from high resolution measurements) $C_{24}H_{14}$. These compounds could be dihydrocoronenes. However, no coronene was found in any of the samples. Sample H, contained in addition to PAH, a range of fatty acids such as oleic acid.

Table 1 summarises the information produced on the content of coal-tar pitch in deposits lying in water mains. The content ranges from about 0.01% to 39% of the deposit collected.

3.2.2

Estimation of coal-tar pitch in particulate matter isolated from tapwater

The data on coal-tar pitch in tapwater is shown in Table 2. Samples N, P, Q and R gave weights of particles in the range 10.2 to 250 mg per 1200 litres. The coal-tar pitch particulate matter

in these drinking waters was 7 ng/l or less. (7 ng/l could be equivalent, however, to 7000 one micrometer diameter coal-tar pitch particles).

Sample M produced a relatively huge amount of particulate matter (17.7 g per 1000 litre). This revealed about 150 ppm (~ 0.02%) of coal-tar pitch (around 2.6 mg per 1000 litres or 2.6 µg per litre) which could be equivalent to about 3 million one micrometer diameter coal-tar pitch particles. Data from a sample of particulate matter collected from an in-line filter on the drinking water service pipe at Medmenham over a period of many months suggested a concentration (average) of around 3 ng per litre coal-tar pitch.

The main problem is deciding how anomalous is sample M which exhibits extremely high recovery of particles with a relatively high concentration of coal-tar pitch. However, without more data on a much wider range of tapwaters it is impossible to gauge the frequency of such an occurrence. As yet no particular characteristics have been found concerning this system that could be linked to the findings.

3.3

Conclusions

The aim of the work was to determine the extent to which drinking water is contaminated with coal-tar pitch particles. Owing to the time needed to develop and test suitable techniques and the slowness of the methods that emerged, a wide survey of drinking waters was not feasible. However, in the limited number of tapwaters examined one sample exhibited high levels of coal-tar pitch.

Mains deposits frequently contain relatively massive levels of PAH due to the presence of coal-tar pitch particles. Coal-tar pitch particles down to at least 3 µm diameter were detected and

one would expect such particles to be "mobile". Clearly, any situation that disturbs the deposits, such as mains renovations etc could release coal-tar pitch particles in the water. Such situations need to be examined.

Several questions need to be considered. Firstly, does the frequent occurrence of high concentrations of coal-tar pitch (and constituent PAH) in mains deposits pose any foreseeable hazards. Secondly, how significant are the high concentrations encountered in sample M (tapwater). Finally, can levels of less than or equal to 7 ng per litre coal-tar pitch (tapwaters N, P, Q and R) be regarded as innocuous.

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Table 1. Analysis of extracts of deposits collected from water mains

Sample	Sample origin	Solubility of deposit in CH ₂ Cl ₂ (%)	Amount of fluoranthene in deposit (ppm)	Estimated amount of coal-tar pitch in deposit
A1	Mains flushing	*	600	1.1%
A2	"	*	46	0.09% (850 ppm)
A3	"	*	15	0.03% (280 ppm)
B1	"	*	6	0.01% (100 ppm)
B2	"	*	15	0.03% (270 ppm)
B3	"	*	26	0.05% (470 ppm)
C	Dirty water problem	*	4 200	7.8%
D	"	75 (1)	ND	ND
E	Air scouring exercise	17	21 200	39%
F	"	4	2 000	4%
G	"	21	15 000	28%
H	Hydrant flushing	3	900	1.8%
J	"	1.8	1 100	2.2%
Coal-tar pitch	New pipe	53	54 000	-

ND Not Detected. Additional analyses indicated bitumen (i.e. petroleum origin)

(1) Cyclohexane used

* Not estimated

Table 2. Analysis of extracts of particles isolated from tapwater

Sample	Sample volume (m ³)	Wt. of particles isolated	Approx. amount soluble in CH ₂ Cl ₂	Amount of fluoranthene (ppm) in particles	Approx. level coal-tar pitch in particles isolated	Approx. level coal-tar pitch in water sampled (per litre)
L	1.0	19 mg	NM	ND	<39 ppm	<~1 ng
M	1.0	17.7 g	1.0%	8(2)	150 ppm (0.02%)	2.6 ug
N	1.2	10.2 mg	10%	ND	<500 ppm (0.05%)	<5 ng
P	1.2	145 mg	3%	2	40 ppm	5 ng
Q	1.2	146 mg	0%	3	60 ppm	7 ng
R	1.2	250 mg	0%	1	20 ppm	4 ng
K(1)	~3000	18 g	6.6%	25	460 ppm (0.05%)	3 ng

(1) Particles trapped by in-line filter

(2) Estimated from pyrene because of interference on fluoranthene peak

NM Not measured

ND Not detected

APPENDIX A

METHODS OF COUNTING PARTICLES IN FLUID STREAMS

A.1 GENERAL PRINCIPLES

The instruments discussed below rely on a particle changing the physical properties of an "interrogation zone". Thus as a particle passes through the zone it may alter the electrical resistance, or light transmission, or light scattering or acoustic properties of the zone.

Some problems seem to be common to all instruments. When more than one particle occupies the zone a loss in the primary count occurs while giving a "secondary count" gain because two small particles will be measured as a single large particle. This problem can be overcome by sample dilution or statistical correction based on some assumptions (The Review of Scientific Instruments 1972, 43(10), pp 1407-1412). In some instruments the passage of a particle through the zone temporarily desensitises the zone for following particles. The interrogation zone is not necessarily isotropic so that the response may vary depending on the path of a particle through the zone.

Counters are calibrated against standard materials whose dimensions have been measured microscopically but there is no independent way of checking the number of pulses. It is assumed that one particle produces one pulse and that every pulse is counted in the correct channel.

A.2 ELECTRIC-ZONE INSTRUMENTS

The best known instrument of this type is the Coulter Counter. Here a suspension of particles in electrolyte is sucked through an orifice.

Electrodes on either side of the orifice measure the changes in resistance of the electrolyte within the orifice due to volumetric displacement of electrolyte by particles. The size range measured is from about 1 μm diameter to about 200 μm , but this range requires several orifices of different sizes because each orifice can only be used for particles 3 to 40% of its nominal size. Counting runs can take only a few seconds but then changing orifice probes and resetting the apparatus takes several minutes. Each orifice probe has to be calibrated and matched to the measuring circuit and must be kept clean. The interrogation zone, being a physical entity, ie a cylinder bounded by quartz, is liable to blockage by large particles.

The orifice is anisotropic and particles passing close to the walls give a different sized and shaped signal from particles passing near the axis. Some counters can recognise and edit out signals from particles near the wall. It is also possible, by hydrodynamic focussing, to arrange for all the sample to pass close to the axis and for a sheath of clean water to pass close to the walls. The instrument measures the volume of a particle but generally prints out the equivalent spherical diameter.

Possibly the biggest disadvantage of electric-zone counters is the need to make the sample conducting by adding electrolyte. This procedure can modify the particles and also be a source of additional particles.

A.3 SONIC-ZONE INSTRUMENTS

There are several types of acoustic particle counters, none of which seems to have become very popular. An instrument developed at the Sperry Co about 1960 uses ultrasonic echo location for counting particles down to 25 μm diameter. One advantage of the instrument is that it would work in opaque, non-conducting solutions. Another instrument measured the power loss of an ultrasonic beam caused by interaction with particles to count and determine the average size of particles.

A.4 PHOTO-ZONE INSTRUMENTS

Photo-zone instruments either measure the decrease in intensity of a beam of light caused by a particles's shadow (light blocking instruments) or measure light scattered by the particle. There are many geometric arrangements of light scatter instruments and different geometries are said to be suitable for different purposes; some instruments measure light scattered at angles close to the forward direction of the beam, others measure backscattered light and others at angles in between. The light scattering properties of a particle depend on its dimensions, shape, refractive index and the wavelength of light used in the experiment. When the wavelength of light is comparable with the dimensions of the particles under study the scattering properties change very rapidly with particle size. However, the shadows of particles larger than about 1.5 μm diameter are proportional to the areas of the particles and for this range light blockage instruments have linear calibrations. (They are also useable for smaller particles but the calibration is no longer linear).

The interrogation zones of these instruments are optically defined and therefore, if properly defined, they should not suffer from wall effects.

However, it is possible for part of a particle to move through the zone.

A.5 CONCLUSIONS

Coulter-type counters require some sample preparation in contrast to photo-zone instruments. The data from different types of counter will not necessarily agree on the same sample. This is because different properties, such as shape, have different effects on the measurements and statistics of size distribution calculation. Particle shape is particularly important in considering light scattering properties. It would be expected that all commercial instruments would agree quite closely as to the number and size of particles in a suspension of narrow-sized ranged spheres. The further real samples are removed from this ideal the greater the differences in the data generated by different instruments.

For the purposes of the current project a light-blockage instrument was considered the best choice. A Kratel Partoscope F seemed especially suitable as it is simple and rapid to operate. Samples require no pre-treatment and several replicate counting runs can be carried out in a few minutes.

A.6 PRACTICAL EXPERIENCE OF THE KRATEL PARTOSCOPE F ED-MP

The instrument consists of three parts: mainframe, pump and sensor. The mainframe contains the printer, data output controls, pump timer programmer and the power supply for the sensor lamp. In addition to the printer, data output is available at an RS-232 interface port. The pump draws sample through the sensor cell. The speed of the pump is controlled at the pump unit but its periods of operation are set on the mainframe. The

sensor contains a quartz/halogen lamp, sample cell and photodiode detector. Particles are counted into 32 size-range channels. The size-range limits for each channel (primary calibration) and the corresponding print-out information are pre-programmed into the machine on a Read Only Memory (ROM) by the manufacturer. The choice of channels to be read and the sampling times are set by the operator on a microprocessor.

The maximum concentration of particles that can be counted without coincidence is 3000 ml^{-1} . Freshly drawn laboratory tap water approached this figure, although on standing the count dropped by 50% in 2 hours and by 80% in 3 days due to settling of heavy particles and, perhaps, disappearance of air bubbles which can also be counted by the instrument.

In practice the instrument was easy to use and able to produce replicate data quickly. However two problems were apparent:

- (a) The sample feed system did not deliver a constant volume. The best relative standard deviation achieved for 10 ml samples was about 2% with a thoroughly warmed-up pump. Used intermittently the variation was worse than this.
- (b) Some of the channels appeared to be wider than their quoted sizes. This has been determined from results obtained in experiments with latex spheres of known size distribution and in experiments on tapwater. In the latter case there is no reason to suspect that, on average, the size distribution should be other than a smooth curve with particle numbers increasing towards the small end of the size range. In practice the measured distributions showed distinct steps.

The instrument was bought to perform specific tasks during the project. Its performance was adequate for these tasks. If the instrument was to be used in other applications it may be necessary to examine aspects of its performance, such as those mentioned above, more rigorously.

APPENDIX B

THE PREPARATION OF LOW-PARTICLE-COUNT WATER

The primary need for low-particle-count water in the project was for water to be used in the handling of samples of particle suspensions.

The best preparation method found was pressure filtration of deionised, distilled water through a filter system consisting of a thick pre-filter, a 0.2 μm pore-size cellulose nitrate membrane (depth type) and, lastly, a 0.1 μm pore-size polycarbonate membrane (surface type). The membranes were held in a commercially-available holder and separated by gauze discs. Advice from various sources stated that pressure filtration generally gives better results than vacuum filtration. The laboratory tapwater, although initially giving good results, developed a precipitate on standing. Deionised water was not a good source of water because it contains particles of resin which proved difficult to remove.

Table B1 gives particle counting results on a laboratory tapwater sample, the same sample after standing for 3 days and a sample of low-particle-count water. The counting conditions were:

Flow rate	50 ml min ⁻¹
Clean time	3 seconds
Sample time	12 seconds
Sample volume	10 ml

The results show channel number, size range of that channel, average particle count for ten runs and relative standard deviations. Also given are the total particle count (per millilitre).

Some points arise from these results:

- a) There is always some variability between different counts on the same sample, even when the count is high. Some of the variability may arise from changes in sample size (see Appendix A.6) but some is genuine scatter of counts between successive runs.
- b) Settling in quiescent samples can effectively remove particles larger than about 8 μm from the count. Low-particle-count water samples also showed the same effect.
- c) Low-particle-count water was accepted for use if the total count was below 10 ml^{-1} .

Water samples are liable to particle contamination during storage and one source of contamination that has to be avoided is ground-glass stoppers.

Table B1. Results of particle counting on tap water, settled tap water and low-particle-count water

Channel	Size µm	Tap Water		Tap water after 3 days' settling		Low-particle-count water	
		Average No. particles/ 10 ml	rsd* %	Average No. particles/ 10 ml	rsd* %	Average No. particles/ 10 ml	rsd* %
0	1-2	1952.4	4.2	1838.8	3.9	16.4	19.5
1	2-3	6043.1	4.3	2630.9	3.9	35.2	8.4
2	3-4	3846.1	5.4	590.1	4.2	13.1	31.0
3	4-5	3769.0	4.1	225.6	7.0	9.4	39.9
4	5-6	3094.7	5.5	63.2	15.1	6.0	31.4
5	6-7	1750.7	5.1	12.2	30.6	2.6	45.1
6	7-8	1690.7	5.2	3.0	60.9	2.8	49.9
7	8-9	1126.7	5.1	0.8	79.1	2.1	72.6
8	9-10	610.0	6.7	0.1	316	1.1	79.6
9	10-11	639.6	7.7	0.1	316	1.1	100.0
10	11-12	345.3	8.7	0.1	316	0.4	129
11	12-13	317.0	7.5	0	-	0.7	118
12	13-14	185.9	11.3	0	-	0.3	161
13	14-15	177.1	10.9	0	-	0.1	316
14	15-16	113.0	9.4	0	-	0.6	161
15	16-17	82.8	12.2	0	-	0.1	316
16	17-18	67.2	10.9	0	-	0.1	316
17	18-19	62.9	26.0	0.1	316	0.1	316
18	19-20	41.1	23.2	0	-	0.3	161
19	20-22	64.8	15.4	0	-	0.1	316
20	22-40	81.6	44.2	0.1	316	0.4	129
31	>40	2.6	116	0.1	316	0	-
		Total No. particles per ml = 2600		Total No. particles per ml = 540		Total No. particles per ml = 9	

* rsd = relative standard deviation (within batch)

APPENDIX C

CENTRIFUGE PERFORMANCE

C.1 THEORETICAL

Figure A.1 shows the general arrangement of the centrifuge and Figure A.2 shows the centrifuge bowl and the dimensions used in the following calculations.

The motor (1425 rpm) drives the centrifuge bowl at 9100 rpm through a flat friction plate clutch and a 1:6.4 gearbox.

Therefore, it is assumed that, in the worst possible case, a particle reaches the edge of the lowest inclined plane travelling outwards through the water at its terminal velocity. In order to be certain of capture the particle needs to cross the gap, 8 mm, to the outside wall before the stream of water sweeps it out of the exit tubes. In the following discussion the effect of water escaping up the gaps between the inclined planes is ignored. The justification for this is twofold. First, the gap between the planes is narrow so that there is a high chance that a particle entering the gap will be trapped in the stationary boundary layer on the underside of a plane. Second, including the effect of water escaping by this route would increase the residence times given in the table at the end of this section, thus making the capture conditions more lenient. Also ignored are turbulence effects and the effect of increased water pressure in the gap region of the bowl because this can be shown to have a negligible effect on the viscosity of the water. Various calculations have to be made in

order to derive a relationship between the terminal velocity of a particle, its size and the flow rate and residence times in the critical zone.

Therefore:

$$\begin{aligned} \text{Rotational speed of the bowl} &= 9100 \text{ rpm} = 152 \text{ rev. sec}^{-1} \\ \text{or, in angular velocity, } \omega &= 955 \text{ rad. sec}^{-1} \end{aligned}$$

The gravitational acceleration developed in the critical zone

$$\begin{aligned} &= \omega^2 R \\ &= 955^2 \times 0.062 \\ &= 56546 \text{ m. sec}^{-2} \\ &(\text{or } 5770 \times \text{normal gravity}) \end{aligned}$$

At terminal velocity the viscous drag on a particle balances the gravitational force acting on it, which can be expressed with Stokes' Law:

$$6 \pi n r v = \frac{4}{3} \pi r^3 (\rho - \rho_0) \omega^2 R$$

where

$$\begin{aligned} v &= \text{terminal velocity (m. sec}^{-1}\text{)} \\ n &= \text{viscosity of water (} 1.3 \times 10^{-3} \text{ kg. m}^{-1} \text{. sec}^{-1}\text{)} \\ r &= \text{radius of particle (m)} \\ \rho &= \text{density of particle (} 1100 \text{ kg. m}^{-3} \text{ for coal-tar pitch)} \\ \rho_0 &= \text{density of water (} 1000 \text{ kg. m}^{-3}\text{)} \\ \omega^2 R &= \text{acceleration (} 56546 \text{ m. sec}^{-2}\text{)} \end{aligned}$$

The left hand side of the equation gives the drag and the right hand side the effective gravitational force (effective mass x acceleration).

The equation reduces to: $v = 9.1 \times 10^8 r^2$
 or, if v is in $\text{mm}\cdot\text{sec}^{-1}$ and r is in μm (10^{-6} m): $v = 0.91 r^2$

The volume of the critical zone = $d \pi(R^2 - (R^1)^2)$
 = 0.16 litre

Now the following table relating water flow rate to minimum size of coal-tar pitch particle retained can be constructed:

Flow rate		Residence time in gap	Velocity needed to cross gap	Minimum size of coal-tar pitch particle retained	
$1.\text{hr}^{-1}$	$1.\text{sec}^{-1}$	sec	$\text{mm}\cdot\text{sec}^{-1}$	radius μm	dia. μm
100	0.0278	5.76	1.4	1.28	2.56
50	0.0139	11.52	0.69	0.87	1.94
20	0.0056	28.8	0.28	0.55	1.1
10	0.0028	57.6	0.14	0.39	0.8

Thus it is a conservative estimate that at a flow rate of $20 \text{ l}\cdot\text{hr}^{-1}$ coal-tar pitch particles in the region of $1 \mu\text{m}$ diameter should be effectively retained by the continuous centrifuge.

C.2 EXPERIMENTAL

The mechanical performance of the centrifuge was checked by measuring its speed of rotation with a differential opto-electronic tachometer on both sides of the clutch. The outputs from both halves of the tachometer were displayed on a dual trace oscilloscope. The measured speed of rotation was $41 \text{ millise}\cdot\text{rev}^{-1}$, or 1463 rpm. The slippage between the clutch plates was about 1 revolution min^{-1} or 1 part in 1500. Thus the measured performance was slightly better than the original specification, giving a bowl speed of 9334 rpm.

To test the particle retention capabilities of the centrifuge experiments were set up where suspensions in water of latex spheres of known size were centrifuged. Particle counts were made of the original suspension, both before and after the run (from sample remaining) and of the effluent from the centrifuge at three to five different times during the run. There was no point measuring the particle concentration remaining in the centrifuge bowl because:

- a) it was too concentrated for the range of the particle counter,
- b) it was difficult to obtain a homogeneous sample and
- c) the soft latex spheres could have suffered aggregation and/or damage during prolonged treatment at high gravity.

The experimental set up consisted of the water supply held in an aspirator and being fed to the centrifuge by gravity through a short tube. (This is shown in Figure A.4, Appendix D.2, except that there was no need for water to be pumped to the aspirator from a bowser.) The latex spheres used were obtained from Duke Scientific (California) and had the properties specified at the head of the relevant results tables below. Three different sizes were used, 4.1 μm , 3.00 μm and 2.02 μm mean diameter. Because of their differences in density from coal-tar pitch these latex spheres correspond in terms of terminal velocity in water to coal-tar pitch spheres of diameter 2.81 μm , 1.97 μm and 1.05 μm respectively. (This was calculated using the equation

$$r_{\text{latex}}^2 (e_{\text{latex}} - e_{\text{water}}) = r_{\text{coal-tar}}^2 (e_{\text{coal-tar}} - e_{\text{water}})$$

Table C2 Results of centrifuging standard latex microsphere suspension as determined by particle counting

A. 4.1 μm (4.9% standard deviation) Styrene-Vinyltoluene microspheres, density 1.047 g.cm^{-3} (Duke Scientific Lot 5236)

Volume passed 9.2 l
 Time taken 50 min
 Flow rate 11.0 l.hr^{-1}

Channel	Size range μm	Influent p/l*	Effluent p/l*	Fraction passed	% Retention
1	2-3	18 600	900	0.049	95
2	3-4	113 800	150	0.0013	99.8
3	4-5	498 000	2200	0.0045	99.5
4	5-6	185 000	550	0.0029	99.7
5	6-7	37 000	530	0.014	98.5
6	7-8	20 900	600	0.029	97
7	8-9	6 100	310	0.051	95
8	9-10	1 308	330	0.253	75

* p/l = particles.litre⁻¹

B. 3.0 μm (3.0% standard deviation) Styrene-Vinyltoluene microspheres, density 1.043 g.cm^{-3} (Duke Scientific Lot 5180)

Volume passed 16.8 l
 Time taken 34 min
 Flow rate 29.6 l.hr^{-1}

Channel	Size range μm	Influent p/l*	Effluent p/l*	Fraction passed	% Retention
0	1-2	17 100	10 900	0.064	95.6
1	2-3	1430 000	136 000	0.095	91.5
2	3-4	148 000	17 900	0.120	88.0
3	4-5	72 000	2 000	0.029	97.1
4	5-6	10 800	1 000	0.097	90.3
5	6-7	1 800	450	0.248	75.1
6	7-8	770	400	0.540	46.0
7	8-9	570	240	0.430	57.0

Table A.2 continued

C. 2.0 μm (0.7% standard deviation) Polyvinyltoluene microspheres, density 1.027 $\text{g}\cdot\text{cm}^{-3}$ (Duke Scientific Lot 5208)

Volume passed 11.1 l
 Time taken 51.5 min
 Flow rate 12.9 $\text{l}\cdot\text{hr}^{-1}$

Channel	Size range μm	Influent p/l*	Effluent p/l*	Fraction passed	% Retention
0	1-2	489 000	152 000	0.311	68.9
1	2-3	850 000	97 400	0.115	88.5
2	3-4	205 000	17 700	0.086	91.4
3	4-5	49 000	10 100	0.206	79.4

* p/l = particles.litre⁻¹

Suspensions were made up by adding a few drops of concentrated suspension as supplied to water (200 ml) and dispersing the suspension in an ultrasonic bath. The dispersed suspension was then added to more dilution water (~20 l) in the aspirator and magnetically stirred.

In the first experiment dilution water was centrifuged in order to provide data for background corrections. These corrections are applied to the data reported in Table C2 by correcting the effluent count in each experiment for the expected leakage of background as determined in this first experiment. The influent count was corrected in each experiment by a measured count on that particular sample of dilution water. The reported influent counts (as particles.litre⁻¹) are background corrected averages of three counting runs on each of two samples. The effluent counts are the average of three counting runs on each of three to five samples taken at intervals during the experiment. It is assumed that each sample of dilution water behaves in the same way, ie the same fraction of particles in each size range is retained, on centrifuging as the sample in the initial experiment. For the channels close to the nominal size of the latex spheres this assumption is not important because the background counts were a very small proportion of the sample counts.

The results are judged to indicate satisfactory performance of the centrifuge and give confidence in its ability to retain coal-tar pitch particles from drinking water.

APPENDIX D

SAMPLE COLLECTION AND PROCESSING

D.1 MAINS DEPOSITS

Samples A1, 2 and 3 and B1, 2 and 3 were collected by flushing at hydrants fitted with plankton nets (~80 µm mesh) and date from 1978. Samples derive either from material caught in the nets (A1, A2 and B3) or fine solids removed from the tank catching water passing through the net (A3, B1 and B2). The samples had been ground to fine powder for X-ray analysis. Sample A1 was taken at the end of a distribution system.

Sample C was collected by a Water Authority and is material removed by swabbing a main with a foam plug.

Sample D is one of a number of similar samples collected in various parts of a distribution system and was suspected to be from a section of the system lined with petroleum bitumen.

Samples E, F and G were collected at hydrants during air-scouring exercises. Sample E is 1.1 g fine material collected from a litre sample of water which passed through a wire mesh trap fitted to the sampling hydrant. Sample F is 25 g of fine material (passing through a plankton net) collected from 6 l water. Sample G was collected in the same way but the yield was about 3 g of hygroscopic material from 6 l.

Samples H and J were collected by flushing at hydrants and both are material caught in the plankton net. In both these cases there was

insufficient material for analysis in the water passing through the nets.

D.2 DRINKING WATER

Samples collected away from the laboratory were collected in a 250 gallon galvanised steel bowser (dimensions given in Figure A.3)

Before filling from a domestic tap the bowser was rinsed with some of the sample water. On returning to the laboratory a special cap (Figure A.4) was fitted to the filler neck of the bowser to allow water to be pumped by nitrogen pressure (maximum 5 psi) from the bowser, via a narrow tube ending close to the bottom of the bowser, to a 20 l aspirator. Pumping was controlled at such a speed as to keep between 8 and 18 l of water in the aspirator while water was running through the centrifuge at about 30 l.hr^{-1} .

The water in the aspirator was stirred magnetically and the flow rate through the centrifuge controlled by a screw clamp on the short length of PVC tubing connecting aspirator and centrifuge.

The process of centrifuging 1.2 m^3 samples took four to five working days. During this time for samples P, Q and R several samples of centrifuge influent and effluent were taken and their particle counts checked. The particle (1 to $220 \mu\text{m}$) removal efficiencies were : Sample P 98.7%, Q 94% and R 98.4%. In each case the effluent from the centrifuge contained less than $5 \text{ particles ml}^{-1}$, ie comparable with the best achievable using the filtration process described in Appendix B.

At the end of the run low-particle-count water (20 l) was used to rinse the bowser and aspirator. The centrifuge bowl was opened. The suspension of

particles (~420 ml) was transferred in several stages to two centrifuge tubes and centrifuged in a conventional bench top centrifuge. After each stage the supernatant liquid in the centrifuge tubes was filtered through silver membrane filters (0.8 μm pore size, prewashed in dichloromethane). Low-particle-count water was used to rinse out the bowl. Thus, at the end of this process the collected solids were distributed between two centrifuge tubes and several silver membranes. The samples were dried and weighed (results in Table 2).

APPENDIX E

ANALYSIS OF MAINS DEPOSITS AND PARTICLES ISOLATED FROM TAPWATER

E.1 EXTRACTION

The aims of the extraction process are to dissolve out PAH from a matrix which may be highly mineralised and, secondly, at the end of the process to detect any weight loss in the sample.

In early experiments methanol and cyclohexane were used as the solvent, but in all later experiments dichloromethane (Rathburn, distilled-in-glass grade) was used because it dissolved a greater fraction of coal-tar pitch (53%) than cyclohexane (43%), and is easier to concentrate because of its lower boiling point.

Mains deposits and particles from drinking water were extracted in the same apparatus. This apparatus, shown in Figure A.5, allows hot solvent to percolate through the sample continuously. Amounts of sample used varied between 100 mg and 2 g for the deposits and 8 mg to 150 mg for particles from drinking water. (Sample M [drinking water] was an exception in that 17 g particles was available for extraction in a normal Soxhlet apparatus). Before performing an extraction the apparatus was cleaned by running two blank extractions for three hours each. Extractions were carried out with 100 ml solvent, except for samples P, Q and R where only 50 ml was used, and run for three to six hours.

After cooling and being allowed to drain the extraction thimble and its contents were dried in a vacuum desiccator. The extract, ie the

dichloromethane solution, was reduced in volume to about 5 ml on a rotary evaporator, transferred to a 10 ml volumetric flask and made up to volume with dichloromethane. Extracts were stored in a freezer until analysed.

The extracts of the mains deposits were generally dark brown, with most of the colour going into solution in the first few minutes of the extraction. Extracts of particles from drinking water were generally colourless except sample R which had a light straw colour.

E.2 GAS CHROMATOGRAPHY (GC)

Extracts were analysed for the presence of fluoranthene and pyrene using capillary column GC under the following conditions:

Early Work:

GC - Carlo Erba 2150 with flame ionisation detection(fid)
Column - 30 m OV-1 fused silica or 15 m OV-1 fused silica
Injector - Grob-type in splitless mode
Carrier Gas - Helium at 1.25 ml.min⁻¹
Temperature
Program - Room temperature to 100 °C, hold 6 min, 5 °C min⁻¹ to 250 °C.

Later Work:

GC - Varian 3700 with fid
Column - 50 m OV-1 fused silica or 15 m Dexsil-300 fused silica
Injector - Splitless with septum purge
Carrier Gas - Helium at 1.5 ml min⁻¹
Temperature
Program - 20 °C for 1 min then 8 °C min⁻¹ to 240 °C

Recorder: Hewlett Packard 3390A integrator

Calculation Method - with Carlo Erba, manual comparison of peak areas with areas of peaks from standards, with Varian, automatic external standard method.

The more precise temperature control of the Varian instrument, and hence exactly repeatable retention times, allowed the use of the automatic external standard method for calculating the amounts of fluoranthene and pyrene from peak areas in sample runs. Chromatograms of extracts of coal-tar pitch have a characteristic pattern, but are so complex that there are no convenient "windows" in which to insert an internal standard. The external standard was a dichloromethane solution of fluoranthene and pyrene, 5.55 and 3.03 ng. μl^{-1} respectively in the early work and 9.99 and 10.2 ng. μl^{-1} respectively in later work.

Fluoranthene and pyrene were separated by 30 to 50 seconds after 20 to 30 minutes, depending on the column in use. Solvent and procedural blanks showed no interferences in the region of interest.

Initial injections of samples were generally of 1 μl from 10 ml and, based on the results of these initial runs, the extract was either diluted or concentrated so that 1 μl injections gave, if possible, between 1 and 100 ng of fluoranthene and pyrene on column.

The results are given in Table E3.

E.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GCMS)

GCMS was carried out on some samples using a VG 16F mass spectrometer and DS2000 data system. The GC part of the instrument was a Hewlett Packard 5710 set up for use with fused silica capillary column whose exit is directly into the EI source of the spectrometer. The GC was fitted with an SGE on-column injector.

Mass chromatograms of m/z 202 indicated the positions of fluoranthene and pyrene in the total ion current traces.

E.4 FIELD DESORPTION MASS SPECTROMETRY (FDMS)

FDMS, performed on a VG ZAB instrument, was used to examine extracts of mains deposits without prior chromatographic separation. The presence of PAH, derived from coal-tar pitch, was indicated by a series of ions at m/z 178, 190, 192, 202, 216, 228, 242, 252, 266, 276 and 278. The spectra also revealed considerable amounts of less volatile and higher molecular weight material in mains deposits which was not evident from GC and GCMS.

Table E3. Results of GC and GC-MS analysis of mains deposits and particles isolated from tapwater

Sample	Weight Extracted (mg)	Volume Of Extract (ml)	Concentration Factor*	Volume Injected (ml)		Measured Amount Of Fluoranthene On Column (ng)		Calculated Concentration Of Fluoranthene In Original sample (ppm)		Mean Calculated Concentration of Fluoranthene in Original Sample (ppm)
				GC	GCMS	GC	GCMS	GC	GCMS	
Deposits										
A1	1489	10	1 0.05 0.05 0.5	0.9 1.3 1.25		106 5.6 5.6		290(b) 379 623		601
A2	1206	10	1 1 1	0.75 1.0 1.3	2	4.3 5.0 7.4	-20	48 42 47	-80	45
A3	1030	10	1 1 1 4	2 2.05 2.4	2	3.2 3.0 3.9		15 14 16		15
B1	541	10	1 5.9 5.9 5.9 33	1.8 1.15 1.45 1.6		ND 1.5 2.3 3.6		4.2 4.9 7.0		5.4
B2	418	10	1 20 20 33	2 1.9 1	3	0.5 19.5 14.4		5.6(h) 12.2 17.2		15
B3	1962	10	1 1 1	1.65 1.7 1.5		8.7 8.5 7.1		27 26 24		26
C	1251	10	1 0.025 0.025 0.025	0.95 1.0 0.8 0.7		555 13.6 11.6 7.8	(b)	4350 4640 3580		4200
D	85	10(a)	1		2		ND (d)			
E	930	180	1	1	1	110	✓ (b)	21000		
F	861	10	0.05 1	0.95	1	8.3	✓ (c)	2000		
G	191	10	0.1	1		29.4	(c)	15000		
H	723	10	0.05	1		3.3	(c)	900		
J	1626	10	0.05	1		8.8		1100		
Particles From Tap Water										
K	1332	10	1 1 1 1	1.0 1.1 1.2 1.0	2	3.0 3.5 4.3 3.3	✓ (b,c)	22.8 24.2 26.6 25.1		24.7
L	11	10	1	1		ND(<0.04)(g)	(b)	<40		
M	17400	10	1 0.05	1 1	1	15? (p=20) - (p 0.7)	✓ (e)	p=11 P= 8		
N	10.2	10	1 20	1 1	1 1	ND ND	ND ND	ND ND		
P	117	10	1 15 15 20	1 1 1	1 1	ND 1 (f) 0.6 (f)	ND 0.54	6 4	2.3	
Q	115	10	1 15 15 20	1 1 1	1 1	ND(<0.2) 1.1 (f) ND	ND 0.65	6.4	2.8	
R	211	10	1 15 20	1 1	1	ND 1.1 (f)	2.2	3.3	1	

NOTES

* Concentration factor = fractional volumetric change of volume of original extract before injection.

1 = aliquot of original extract injected
 <1 = sample diluted
 >1 = sample concentrated

P = Pyrene
 ✓ PAHs usually present in coal-tar pitch recognised in the spectra.
 ND = Not Detected

- (a) Sample extracted with cyclohexane
- (b) Sample also examined by LAMPA
- (c) Sample also examined by PDMS
- (d) Sample examined by liquid chromatography
- (e) GCMS revealed interference on the fluoranthene peak.
- (f) Peak of correct retention time seen. Accuracy of integration doubtful due to nearby peaks of similar strength
- (g) High sensitivity, high noise settings. Noise = 4% fsd = 0.04 ng
- (h) Preliminary runs either overloaded or insufficient sample for reliable integration. Not included in calculation of mean

APPENDIX F

LAMMA

F.1 INTRODUCTION

Some samples were taken to Leybold-Heraeus GmbH in Cologne in order to examine them using a LAMMA 500 laser microprobe mass analyser. At the time of the visit several mains deposit samples were available but only two early samples from the tapwater particle series.

F.2 PRINCIPLE OF LAMMA

The instrument uses a laser to vaporise and ionise small areas of sample. The ions formed are collected and separated according to their mass to charge ratio (m/z) in a time-of-flight mass spectrometer. The optical system uses a microscope to focus both a low-power pilot laser, which pin-points the target area in the sample, and high-power, vaporising laser on the sample. The target area can be as small as $0.5 \mu\text{m}$. Additional optics allow the whole sample to be viewed by incident or transmitted light while the sample is manipulated in the vacuum chamber. After the laser pulse any ions formed are collected by an electrostatic lens system and accelerated into the spectrometer. Either positive or negative ions can be studied, depending on the polarity of the collecting lens. Signals from the ion detector are collected by a fast transient recorder and either reproduced directly as a spectrum on a strip chart or fed to a data system.

Samples are analysed in the transmission mode, that is the laser beam hits one face of the sample and ions are extracted from the opposite face. This

geometry limits the thickness of samples that can be examined to a few microns or to areas at the edges of thick samples. This is no disadvantage for the original purpose of the instrument which is to examine thin biological sections. A new instrument (LAMMA 1000) has now been developed which will allow examination of the surfaces of larger and thicker samples.

The LAMMA 500 has been used to examine a wide variety of samples. It appears to be effective for metals, salts and those organics having low ionisation energies. Quantitation depends on the use of standards but is complicated by matrix effects.

There are approximately a dozen instruments in commission around Europe and the USA, but there are none in the UK.

F.3 ANALYSIS OF WRc SAMPLES

F.3.1

Particles of coal-tar pitch scraped from a cast-iron pipe

Basically two different types of spectra were obtained. Type A was typical of a mixture of polycyclic aromatic hydrocarbons (PAH) with clusters of ions in which the most intense are the molecular ions of groups of isomers at m/z 178 (phenanthrene and anthracene), 202 (flouranthene and pyrene), 228 (benz[a]anthracene and chrysene), 252 (benzopyrenes, benzofluoranthenes and perylene) and 276 (indenopyrene and benzoperylene). Also seen are the ions of methyl-PAHs at m/z 216, 242 and 266. Type B spectra were of carbon clusters with ions at m/z $(12x + y)$, where x is the number of carbon atoms present with values 1 to 16. and y is the number of hydrogen atoms with values 0 to 6. The largest peaks were for ions where $x = 5$ to 7 and in most clusters, especially where x was even, the $y = 2$ peak was the strongest. For example in

the cluster starting at m/z 72 ($x = 6$) the m/z 74 peak of C_6H_2 was the largest of the group. Where x was odd the $y = 1$ and 3 peaks were also strong.

F.3.2

Particles from drinking water retained by an in-line filter (Sample K)

Positive ion spectra showed the following ions, some of which can be assigned to metals and metal oxide clusters:- m/z 7 Li, 23 Na, 24 Mg, 27 Al, 28 Si, 39 & 41 K, 40 & 44 Ca, 48 Ti and/or Ca, 54 Fe?, 55 Mn, 56 Fe and CaO, 57 Fe and CaOH, 59 Co, 63 & 65 Cu, 72 FeO, 73 FeOH, 75 As, 83 & 85 FeAl or $Mg_2Cl?$, 88 Sr or Si_2O_2 , 96 Ca_2O , 103, 112 Fe_2 or Ca_2O_2 , 113 Ca_2O_2H , 119, 128 Fe_2O , 129 FeOH, 152 Ca_3O_2 , 155, 159, 168 Ca_3O_3 , 169 Ca_3O_3H , 175, and 206, 207 & 208 Pb and 208 alone Ca_4O_3 .

Negative ion spectra showed ions at m/z 16 O, 17 OH, 19 F, 26 CN (a common instrumental artefact), 32 O_2 or S, 35 & 37 Cl, 42 CNO (artefact), 43 AlO, 59 AlO₂, 63 PO₂, 72 FeO, 79 PO₃, 88 FeO₂ or Si_2O_2 and 119 CaPO₃. The ions at 63 and 79 are characteristic of phosphates. There was no evidence for sulphate and very little for silicates in this sample. Carbonates do not give characteristic ions.

No evidence for PAH was found in the small number of particles examined although by gas chromatographic analysis the sample contained 25 ppm fluoranthene.

F.3.3

Particles of mains sediments obtained by flushing at hydrants (Samples C & E)

Several particles from two samples were analysed. Some small particles down to about 3 micron diameter appeared to be pure PAH, other particles were mixtures of iron and PAH and some purely inorganic, mainly iron and calcium. One spectrum, in addition to iron and calcium species, also showed carbon cluster ions. One small particle

contained lead and bismuth. In some particles traces of copper, zinc, manganese and bromine were observed. All these spectra were run from m/z 50 upwards and therefore light metals, including calcium, could not be directly observed.

F.3.4

Particles suspected to be mostly petroleum bitumen (Sample D)

No PAH were observed. Carbon cluster spectra were seen and traces of the following elements:- sodium aluminium, potassium, calcium, vanadium? and iron and/or calcium oxide.

F.3.5

Particles collected by centrifugation of stored drinking water (Sample L)

The positive ion spectra of several particles of this sample showed the presence of lead, bismuth, tin (m/z) 116, 117, 118, 119 and 120), indium (m/z 115 and weak 113), zinc, copper, iron, manganese, calcium, potassium, silicon, aluminium and sodium. The occurrence of lead, tin and indium together suggests that the source of some of these particles was a bearing. The negative ion spectra showed evidence for phosphate, silicate and chloride.

F.4 CONCLUSIONS

Compared to other surface analysis techniques LAMMA is undemanding in terms of sample preparation and high vacuum requirements.

Spectra can be obtained of metal ions, metal ion oxide and salt clusters and some organics. Negative ion spectra of common salt anions are seen. Carbon clusters can be observed from the pyrolysis of organics in both negative and positive ion modes.

The technique may have several applications in the water industry, for example, analysis of lead deposits, filter muds, river sediments, flocs, sludges, paints, concretes and plastic pipes.

Coal-tar pitch is easy to recognise by its LAMMA spectrum and spectra can be obtained from 30 pg particles.

The ability of the new LAMMA 1000 instrument to handle larger samples may make it possible to scan systematically arrays of particles. With the addition of automated scanning and peak recognition software it might be possible to count and size coal-tar pitch particles in matrices of other particles.

Leybold-Heraeus are aware of our desire for this type of development which should be further discussed at WRc, the Department of the Environment and with other parties interested in the project.

APPENDIX G

IMAGE ANALYSIS

Image analysis is the name given to the technology of storing the image of a specimen in digital form by storing light intensity of the image at each picture point ("pixel") and then extracting quantitative geometric and densitometric information from the stored image. Many different types of instrument are available, differing in the degree of automation, capacity, computer assistance and software development.

The original image can be presented in several different ways, eg photograph or microscope, but is generally transmitted to the digitising computer by way of a video camera system or light pen. The image can be stored in up to 600 000 picture points, each of a specified grey level. (No doubt the incorporation of real colour will soon be available). Once stored the image can be manipulated, depending on the software available, to output modified images (eg deleting unwanted features on the basis of contrast, size, shape etc), or have pseudo-colour added. Features of the image can be sized, counted, have their distribution calculated and areas, chords, major/minor chord ratios, and perimeters measured. Fawell⁽¹⁾ describes the use image analysis with these measurements and other functions to sort marine zooplankton.

Image analysis is being used in many fields of research where it is useful to describe the appearance of a sample in quantitative terms.

REFERENCE

FAWELL J K (1976) In: Zooplankton, fixation and preservation, edited by H F Steedman, Paris, Unesco Chapter 7, p201-206.

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