

# Particles in Hot Gases—Sampling and Sample Preparation

The following are summaries of two of the papers presented at a Meeting of the Particle Characterisation Group, held on June 10th, 1987, at the Health and Safety Executive, 403–405 Edgware Road, Cricklewood, London N.W.2.

## Smoke Particles and their Optical Properties

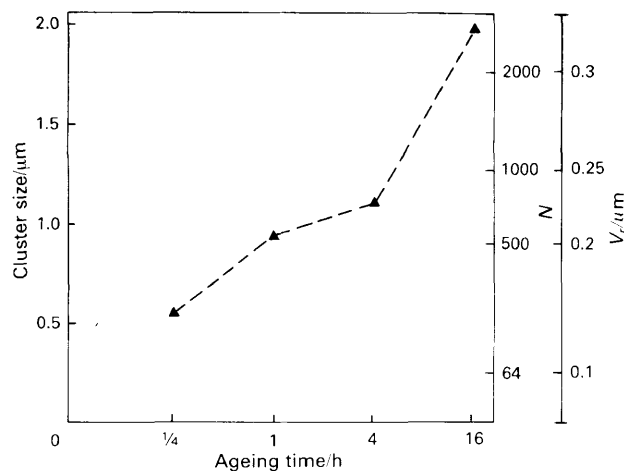
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Smoke is typically a heterogeneous mixture of particles of different sizes, structures and composition. High-temperature, flaming combustion produces black sooty smoke whereas white, oily smoke is formed by low-temperature, smouldering combustion. The environmental effects of smoke in the atmosphere, such as visibility reduction, air pollution and the so-called Nuclear Winter are predominantly caused by sooty smoke. Although their mass concentration is small compared with other particles in the atmosphere, these smoke aerosols have the unusual property of strongly absorbing light of visible wavelengths, but transmitting light of infrared wavelengths. This behaviour is central to the alteration of climate but the exact properties vary according to the origins of the particular smoke.

### Optical Properties

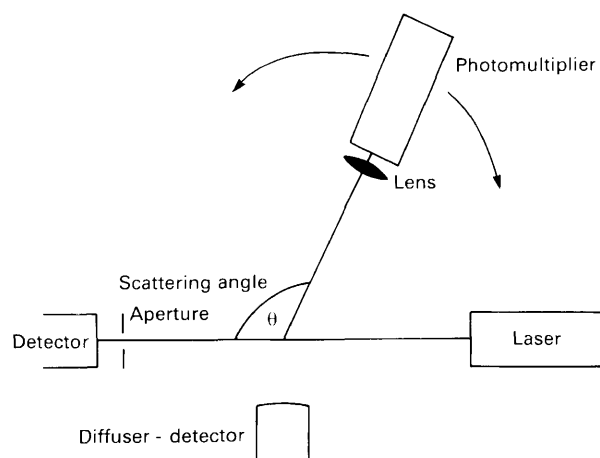
The optical properties of smoke are functions of chemical composition, morphology and particle size. The composition depends on the type of fuel and the conditions under which it is burnt. The morphology and size are determined by formation processes and subsequent microphysical processes (e.g., coagulation and absorption of water vapour). As the physical properties of the particles are changing with time, the optical properties also change with time.



**Fig. 1.** Variation in morphology of carbonaceous smoke with ageing time, determined from SEM investigations.  $V_r$  is the equivalent volume radius

It has been traditional to use the Mie theory for homogeneous spheres to calculate the optical coefficients of

atmospheric particles. This enables the variation of absorption with particle size to be modelled, assuming that they are spherical. It suggests that the extinction should decrease linearly with the size of the spherical aggregate, beyond a radius comparable to the wavelength. However, the shape of smoke particles can be fairly complex. Laboratory studies of black sooty smoke have shown it to be in the form of branched-chain agglomerates composed of smaller spherules. These fluffy clusters of spherules are up to 20 μm in total length, whereas the individual particles are all of roughly equal size, about 20–50 nm in diameter. Previous workers have converted the measurements of agglomerate size to an equivalent



**Fig. 2.** Schematic diagram of experimental layout

volume diameter and then used the Mie theory. Recently, Berry and Percival<sup>1</sup> have developed a theory for light scattering from fluffy particles, based on the assumption that they consist of fractal aggregates of spherules, each spherule being significantly smaller than the wavelength of light. For a cluster containing  $N$  particles all of radius  $a$ , the cluster size,  $R$ , is given by  $R = aN^{1/D}$  where  $D$  is the fractal dimension. If  $D = 1$ , then the spherules are formed into straight lines, if  $D = 2$  they are in sheets and if  $D = 3$ , they are in a solid spherical shape, as assumed by the Mie theory. Computer models and measurements have shown the smoke clusters to have a fractal dimension of 1.78. Fractal theory predicts that when smoke coagulates in clusters of  $D < 2$  the absorption of light is hardly changed and that the scattering per spherule initially increases and then levels off at a value exceeding that of an isolated spherule.

## Experimental

Experiments have been performed to study the influence of particle shape and morphology, as a function of time, on light scattering and absorption. Smoke produced from the combustion of liquefied petroleum gas has been sampled on 0.4  $\mu\text{m}$  nucleopore filters and examined by scanning electron microscopy (SEM). From the SEM micrographs, the projected area of the cluster, fractal dimension and individual particle size have been estimated. Hence, the cluster size and number of particles in a cluster can be calculated. Their variation with time is shown in Fig. 1. It can be seen that after 16 h the cluster size has increased four-fold, whereas the number of particles in a cluster has increased approximately 20 times.

A transmissiometer and integrating nephelometer have been designed to study the effect of coagulation on the optical

properties (Fig. 2). Observations of the molar absorption coefficient, by measuring the direct beam obscuration, appear to show that it remains remarkably constant with time with a value of approximately  $1 \text{ l m}^2 \text{ g}^{-1}$ . Similarly, the single scattering albedo shows no significant trend. Hence, it appears that aggregation does not influence the optical properties. The polar nephelometry indicates the predominance of forward scatter and little change in the asymmetry factor with time. These observations are consistent with the optical theory of fractal smoke, and suggest that the absorption of light by smoke is hardly affected by coagulation.

## Reference

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# Particles and Sampling from Flames and Flue Gases

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The studies described here are concerned with methods for sampling particles from flames, where temperatures are around  $1500^\circ\text{C}$ , and from flue gases at the back end of boiler plants where temperatures are likely to be lower ( $120\text{--}300^\circ\text{C}$ ). In the boiler furnace, carbon burn-out data are required for flame models and heat transfer calculations. At the economiser and after the precipitators, particle concentrations are measured in order to assess precipitator efficiency and the amount and composition of particles going to the chimney.

Combustion equipment that uses gas or light oil as a fuel will, under certain conditions, make smoke. The fine soot particles present, which are made up of carbon with a little hydrogen, will individually be about  $0.05 \mu\text{m}$  in size, although they may form long chains. Where heavy fuel oil is burnt and particularly residual fuel oil (RFO) soot, oil-coke particles and a little ash may be present in the emissions. The coke particles will be mainly in the size range  $10\text{--}100 \mu\text{m}$ . RFO contains only up to about 0.05% ash so that it is the coke and soot that makes up the bulk of the emissions.

For coal-fired boilers, where the ash content of the coal can be up to about 35%, the main concern is with ash particles, although soot and coal chars or cokes may be present. Much of the ash (20–40%) falls to the boiler floor and can be removed but the remainder, apart from deposited material, eventually reaches the boiler exit. Here it can be trapped in cyclones or electrostatic precipitators and only a very small amount ( $<0.115$  grams per normal cubic metre at present) goes on to the chimney.

## Soot Measurements

In the Shell method used here, a stain is produced by drawing the flue gases at a constant differential pressure through a filter-paper. The filter-paper, the differential pressure and the sampling time have been standardised as Whatman No. 4, 3 in Hg (101.6 mbar) and 1 min, respectively. Comparison of the stain with a standard range of shades varying from white to black then yields a Shell smoke number between 0 and 9. This progression from white to black is in equal photometric steps through neutral shades of grey. The smoke scale spot number is defined as the percentage reduction, due to the smoke stain, of reflected incident light divided by ten. Thus, the first spot, which is the colour of the unprinted scale, is zero as there is no reduction in reflected incident light. The last spot on the scale is

very dark and reflects only 10% of the incident light, corresponding to a reduction of 90% and hence a smoke number of nine.

Smoke numbers can be measured by comparison with a printed scale and also by using a reflectometer, the instrument being set to represent 100% reflectance from a clean filter-paper.

In flames, a water-cooled probe with the filter-paper mounted at the inlet end can be used. Matthews *et al.*<sup>1</sup> have described such a probe for use in natural gas flames. The probe is essentially in two parts: a  $1\frac{1}{2}$  in (38.1 mm) o.d. water jacket and a  $\frac{5}{16}$  in (7.9 mm) o.d. sampling tube which fits inside the water jacket and carries the filter-paper. The axial position of the sampling tube in the water jacket can be varied in order to control the temperature of the gases at the filter-paper. Graphs relating carbon concentration to smoke number are reported.

There are a number of continuous automatic smoke density meters on the market using a lamp on one side of the duct and a photoelectric cell on the other. These instruments need to be accurately aligned optically and can be difficult to check for electrical component drift and clean optics. Instruments operating from one side of the duct only have been developed and these can be more easily removed or checked and are not affected by duct distortion. These developments have been summarised.<sup>2</sup>

## Coke and Ash Measurements

### Measurements in Flue Gases

No single instrument will give an automatic indication of the total solids burden in the flue gases. Instruments that are available respond either to small or large particles. The former give the plume its visibility so that they can be measured optically with smoke density meters, but the latter, contributing to ground level deposits, need to be caught before their concentration can be determined.

For measuring the larger particles in the flue gas a semi-continuous permanently installed instrument, called the CERL flue dust monitor, has been described by Snowhill.<sup>3</sup> Here the instrument collects a solids sample by deposition on glass plates mounted in a specially designed cell. Their optical observation is integrated over an interval of some minutes before an air purge re-establishes the zero condition.

In order to collect samples of solids in the flue gas ducts of oil-fired boilers, where the solids concentrations are low, it is usual to use probes with filters (usually silica wool or tyglass bags—*i.e.*, woven glass fibres—although more recently PTFE filters have been used). The filters may be located at the hot end of the probe in the plant, or at the cold end outside the plant. In the latter instance the filter will need to be kept at a temperature above the acid dew point. Three types of probe have been tested, two with filters at the hot end of the probe and one with the filter outside the boiler. The concentrations and size distributions of the material collected were the same in all instances.

On coal-fired plants these filters, with the possible exception of the bags, would block rapidly and miniature cyclones have been used ahead of the filters, *e.g.*, reference 4. Again, the cyclones and filters can be inside or outside the flue gas duct.

### Sampling in Flames

In flames where the temperatures are much greater than the flue gas (1500 °C compared with, say 300 °C) it is necessary to use water-cooled probes. In oil-fired flames the filter can be located at the hot end, because the filter will block only slowly, and manually operated probes for doing this have been described<sup>5</sup> where the filter is made of sintered bronze. However, this type of probe needs to be pulled in and out of the flame each time a sample is taken. It is more convenient to bring the sample to the back end of an internally heated probe (to prevent condensation and the solids sticking in the sample line). This is particularly true in coal flames, because it is usual to use cyclones to collect the solid material, and these cannot be located in the flames. It is possible to use a resistance-heated tube inside a water-cooled probe.<sup>6</sup> This arrangement is complicated, but very necessary to avoid condensation and the formation of sludge in the probe.

Another method that we have used involves cooling the probe with oil, operating at between 150 and 200 °C. In this way the dust-laden gases coming into contact with the probe walls will find surfaces at temperatures above the dew point. The cooling oil used is Transcal SA, manufactured by BP. The oil is capable of operating at bulk fluid temperatures of 320–343 °C and a skin temperature of 370 °C. The vapour pressure is low (0.04 bar at 200 °C) and the oil presents no special handling problems. The probe is fitted with thermocouples for monitoring the metal wall temperature and the bulk fluid temperature. The oil is circulated through a cooling circuit which comprises a

water-cooled heat exchanger, pump, flow meter, expansion tank and valves.

### Particulate Material

The soot - coke mixtures obtained from heavy fuel oils contained up to 8% hydrogen. The other non-carbonaceous material in these mixtures was ash and this ranged from about 14 to 36%. This ash contained many of the constituents present in the original oil; for example, V (27.6), Ni (5.8), Fe (4.2), Ca (4.2), Al (3.6), Na (15.2), Si (13.6), S (25.6), where the values refer to the percentage of oxide present. Most of the material, by mass, was in the size range 10–100 µm. Of course, this will depend very much on the quality of the initial fuel-oil atomisation.

Particles from coal-fired plants contained different minerals from those present in oil, for example, more silica, aluminium, iron and calcium. A detailed comparison has been made of the impurities in oil and coal.<sup>7</sup> Before the precipitators in a coal-fired plant the particles sizes are similar to those from an oil-fired plant (but of a different composition with only about 5% carbon), being up to about 100 µm in size. After the precipitators or at the chimney, sizes are up to only about 20 µm.<sup>8</sup>

The work was carried out at the Marchwood Engineering Laboratories of the Technology Planning and Research Division and the paper is published with permission of the Central Electricity Generating Board.

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