THE DRI THERMAL/OPTICAL REFLECTANCE CARBON ANALYSIS SYSTEM: DESCRIPTION, EVALUATION AND APPLICATIONS IN U.S. AIR QUALITY STUDIES

Judith C. Chow, John G. Watson, Lyle C. Pritchett, William R. Pierson,
Clifton A. Frazier and Richard G. Purcell

Desert Research Institute, P.O. Box 60220, Reno, NV 89506, U.S.A.

Abstract—The thermal/optical reflectance method of carbon analysis developed by Huntzicker *et al.* (in *Particulate Carbon, Atmospheric Life Cycle*, edited by Wolff G. T. and Klimisch R. L., pp. 79–88, Plenum Press, New York, 1982) has been adapted by several laboratories for the quantification of organic and elemental carbon on quartz-fiber filter deposits. While the principle used by these laboratories is identical to that of Huntzicker *et al.*, the details differ with respect to calibration standards, analysis time, temperature ramping and volatilization/combustion temperatures. This paper reports a variation on this method which has been applied to over 27,000 samples taken in more than a dozen urban and regional air quality studies in the U.S.A. In this variation, a 0.5 cm² punch from a filter is submitted to volatilization at temperatures of 120, 250, 450 and 550°C in a pure helium atmosphere, then to combustion at temperatures of 550, 700 and 800°C in a 2% oxygen and 98% helium atmosphere. The carbon which evolves at each temperature is converted to methane and quantified with a flame ionization detector. The seven separate carbon fractions facilitate evaluation of the method and increase the information content concerning the samples.

The reflectance from the deposit side of the filter punch is monitored throughout the analysis. This reflectance usually decreases during volatilization in the helium atmosphere owing to the pyrolysis of organic material. When oxygen is added, the reflectance increases as the light-absorbing carbon is combusted and removed. Organic carbon is defined as that which evolves prior to re-attainment of the original reflectance, and elemental carbon is defined as that which evolves after the original reflectance has been attained. By this definition, "organic carbon" is actually organic carbon that does not absorb light at the wavelength used (632.8 nm) and "elemental carbon" is light-absorbing organic and elemental carbon. Assumptions underlying the procedure are discussed, as well as comparisons with other methods and recommendations for further work.

Key word index: Aerosol, air pollution, organic and elemental carbon, light-absorbing carbon, thermal/optical method, reflectance/transmission, pyrolysis.

INTRODUCTION

Organic and elemental carbon have been found to be significant causes of light extinction and to be major chemical constituents of atmospheric aerosols (e.g. PM2.5, PM10, TSP; particulate matter with aerodynamic diameter (d_p) less than 2.5, 10 or 30 μm, respectively). By examining 1300 aerosol samples collected in 1975 from 66 urban and rural sites in the U.S.A. Shah (1981) and Shah *et al.* (1986) reported that carbonaceous material constituted, on average, 13% of TSP mass; some two-thirds of the carbon was organic, attributed mostly to combustion. In the eastern Midwest in 1980–1981, typically 19% of the TSP mass was carbon (Huntzicker *et al.*, 1986), some two-thirds of which was organic, attributed mostly to combustion. In the Los Angeles Air Basin in 1982, typically 40% of the fine-particle mass ($d_p \leqslant 2.1$ μm) was carbonaceous material (Gray *et al.*, 1986), some two-thirds of which was organic, attributed mostly to primary emissions.

Light extinction by particulate organic carbon occurs primarily through scattering, with efficiency between 2 and 5.5 m² g⁻¹ (Japar *et al.*, 1981; Shah *et al.*, 1984; Trijonis *et al.*, 1988; Watson *et al.*, 1988a,b,c;

Pierson *et al.*, 1989), depending on the relative humidity. Elemental carbon is the major contributor to light absorption (Rosen *et al.*, 1978; Japar *et al.*, 1986; Adams *et al.*, 1990a,b) in the atmosphere, with an extinction efficiency of approximately 10 m² g⁻¹ at a wavelength (λ) of 515 nm and varying as $1/\lambda$ (Japar and Szkarlat, 1981; Szkarlat and Japar, 1981, 1983; Japar *et al.*, 1984b, 1986; Trijonis *et al.*, 1988; Watson *et al.*, 1988c; Adams *et al.*, 1989, 1990a).

Because carbon is such an abundant component of suspended particles (in gram-atoms it is more abundant than is sulfate in gram-moles), simple and reliable methods are needed to quantify it in ambient air samples. At the same time it is important to try to distinguish between organic and elemental carbon because of their differing origins and differing atmospheric chemical and optical properties.

Thermal/optical analysis has usually been used to quantify organic and elemental carbon in source and receptor aerosol samples in air quality studies conducted in the U.S.A. There are several variations on this method with respect to: (1) the temperatures to which samples are subjected, (2) the length of analysis time at each temperature, (3) the rate of temperature

increase, (4) the composition of the atmosphere surrounding the sample, (5) optical monitoring of pyrolysis/volatilization/combustion and (6) calibration standards. As will be shown in this paper, these differences in the application of thermal/optical methods have little effect on the total carbon measured on a sample, but can have a significant effect on the point of delineation between organic and elemental carbon. The same is true for other carbon analysis methods. For this reason, it is essential that any widely used method or variation thereon be properly documented.

The objectives of this paper are:

● to describe the DRI thermal/optical reflectance (TOR) carbon analysis method,
● to evaluate it and compare it to other variations of the TOR method and to other carbon analysis methods,
● to discuss its application in major studies conducted to date.

BACKGROUND

The TOR carbon analysis hardware and procedure are based on the preferential volatilization and oxidation of organic compounds and elemental carbon at different temperatures. The evolution of the concept of thermal/optical analysis is evident in a series of early papers by Novakov and colleagues (Rosen et al., 1977, 1979; Novakov, 1981, 1982). The present DRI version of the TOR method derives from research conducted at the Oregon Graduate Center (OGC, now Oregon Graduate Institute or OGI, Beaverton, OR) since 1975, as well as similar research in other laboratories (e.g. Johnson and Huntzicker, 1979; Cadle et al., 1980a, b, 1983; Johnson, 1981; Johnson et al., 1981; Mueller et al., 1981; Cadle and Groblicki, 1982; Huntzicker et al., 1982; Tanner et al., 1982; Adams et al., 1989; Tanner and Miguel, 1989). The first application of the thermal method to quantifying sources of suspended particulate matter was in the Portland Aerosol Characterization Study (PACS; Watson, 1979) where it was applied, but without the optical feature, to over 1000 source and ambient aerosol samples. The PACS was the first study ever to apply carbon analysis in the development of State Implementation Plans (SIPs) for suspended particulate matter, and it was the first study to identify emissions from wood combustion as a major contributor to urban ambient particulate concentrations. In the PACS, volatilizable (organic) carbon was defined as that which evolved between ambient temperature and 600°C in a 100% helium (He) atmosphere, and non-volatilizable (elemental) carbon was defined as that which evolved at 600°C in a 2% oxygen (O_2)/98% He atmosphere (Johnson and Huntzicker, 1979).

During the PACS analysis it was recognized from the darkening of the samples that, in the absence of O_2, some of the deposit on the filter would char when

temperatures exceeded 300°C. This charred organic material would burn along with the particulate elemental carbon when O_2 was added. Efforts were made with this first-generation carbon analyser to minimize this artifact by dividing the analysis into several temperature ranges. The artifact was minimized when as much carbon as possible was volatilized below 300°C. Without some means to quantify this "pyrolysis" (charring) effect, however, it was found that significant fractions of the organic carbon might be measured as elemental carbon. It is probably true, moreover, that the organic compounds most likely to contribute to the pyrolysis problem are also the ones least removable by volatilization (or by solvent extraction).

After PACS, a second-generation carbon analyser was developed at OGC in which the reflectance of a helium–neon (He–Ne) laser light focused onto the sampling substrate was continuously monitored throughout the analysis (Johnson, 1981; Johnson et al., 1981). The sample was subjected to the following sequence of five conditions: 2% O_2/98% He at 350°C, pure He at 600°C, 2% O_2/98% He at 400°C, 2% O_2/98% He at 500°C, 2% O_2/98% He at 600°C. During analysis, the reflected light intensity normally decreased in He at temperatures exceeding 350°C. By the time the temperature reached ∼600°C, the reflected light intensity had attained its minimum value. Before O_2 was added to the He atmosphere, the temperature of the oven was dropped to 400°C. When O_2 was added, the reflected light intensity increased at a rapid rate. In this second-generation method, "volatile organic carbon" was defined as carbon evolved in 2% O_2/98% He at 350°C. "Residual organic carbon" was defined as all of the carbon which evolved between 350 and 600°C in pure He plus that which evolved at 400°C in 2% O_2/98% He before the reflected light intensity regained its initial value. "Organic carbon" was defined as the sum of volatile and residual organic carbon. The carbon which subsequently evolved at ⩾400°C in 2% O_2/98% He was defined as "elemental carbon". Shah (1981) re-analysed the PACS samples and found that, even though total carbon concentrations were reduced by about 20% because of organic aerosol losses over the 3-year storage period, the elemental-to-total-carbon ratios using the thermal/optical approach were nevertheless lower than those measured during the PACS without optical pyrolysis correction.

Development of a third-generation instrument was initiated by Rau (1986) between 1980 and 1986. The fiber optic system of the present OGI and DRI instruments, as well as many configurational and design improvements such as the present flow control and flow patterns, oven controller, methanator and flame ionization detector (FID) power supply, all date from that work.

With the advent of the federal PM10 standard (Federal Register, 1987a, b), and EPA's guidance (EPA, 1987) to use receptor model source appor-
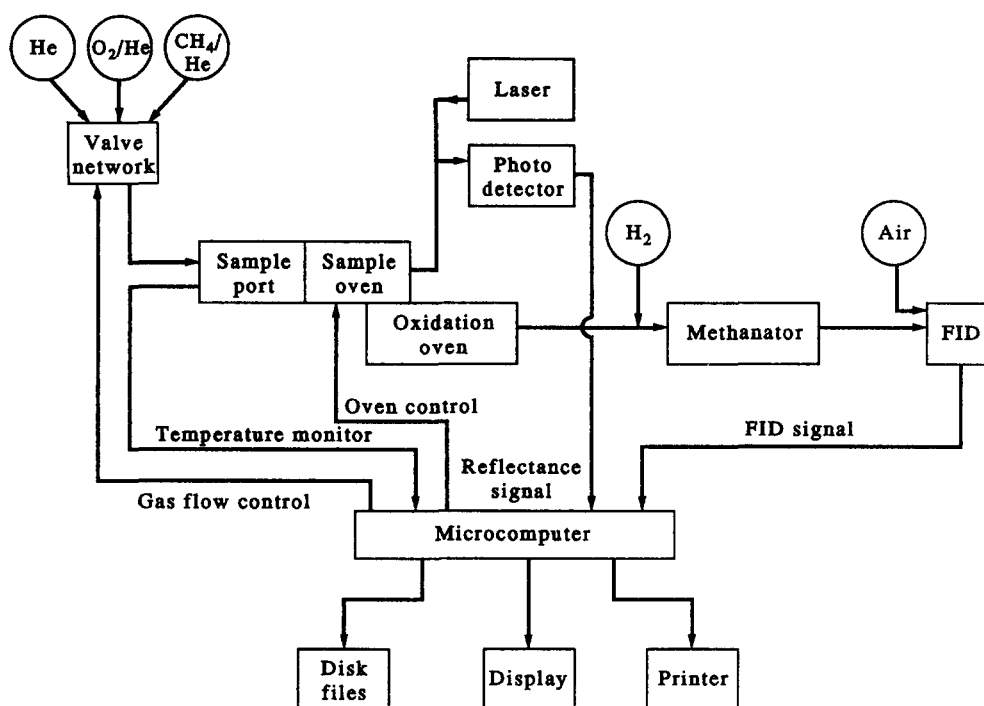
Fig. 1. DRI thermal/optical reflectance carbon analyser block diagram.

tionment to develop emissions reduction strategies, the demand for carbon analysis increased significantly. These demands required better temperature control, sample presentation and reliability than could be provided by the one-of-a-kind research units. The hardware and procedures reported here were developed at DRI to meet those needs. As the hardware has evolved, features have been added which allow substantial flexibility for research into the chemical nature of atmospheric particulate carbon and its measurement. Basic hardware improvements continue to be made as more precise and reliable components become available. These recent improvements enhance efficiency and reliability, but do not affect the fundamental TOR analysis principle.

THERMAL/OPTICAL REFLECTANCE (TOR) CARBON ANALYSER

The hardware for the third-generation TOR instrument built at DRI is shown in Fig. 1. The configuration of the volatilization/combustion area is shown in Fig. 2. Figure 3 is a photograph of the instrument. Except for the software and specific temperatures used, its operating details are very similar to the present OGI system.

The analyser operates by: (1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch taken from a quartz-fiber filter, (2) converting these compounds to carbon dioxide (CO_2) by passing the vola-

tilized compounds through an oxidizer (MnO_2 at 912°C), (3) reduction of the CO_2 to methane (CH_4) by passing the flow through a methanator (firebrick impregnated with nickel catalyst at ~550°C in a stream of hydrogen) and (4) quantification of CH_4 by FID.

The correction for pyrolysis is made by continuously monitoring the filter reflectance (via a He–Ne laser at a wavelength of 632.8 nm and a photodetector) throughout an analysis cycle. This reflectance, largely dominated by the presence of elemental carbon and light-absorbing heavy organic materials, decreases as pyrolysis takes place and increases as light-absorbing carbon is burned during the latter part of the analysis cycle. By monitoring the reflectance until it returns to its initial value, the portion of the elemental carbon peak corresponding to pyrolysed organic carbon can be assigned to the organic fraction. A 632-nm bandpass filter is used to block light emitted by the sample oven from reaching the photodetector.

Samples that are intended for carbon analysis are collected on quartz-fiber filters that had first been heated in air at 900°C for 3 h to lower the blank. For routine analysis, a 0.5 cm² circular punch is removed from the filter and placed vertically into a quartz boat, which is inserted into the oven area with a thermocouple that also serves as a pushrod (see Fig. 2). The system after sealing is first flushed with He for 4 min to remove any residual oxygen. It is imperative also that there be an in-line scrubber to remove the last traces of O_2 from the He coming out of the gas cylinder. A microcomputer controls the valves and the oven
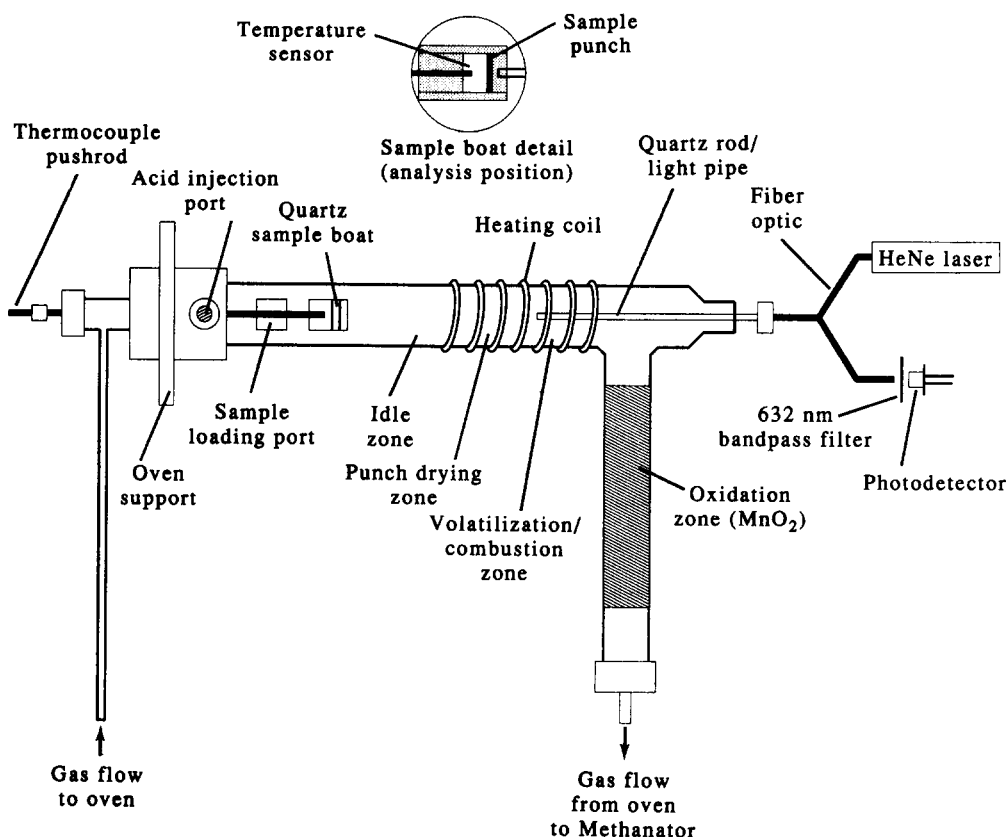
Fig. 2. Volatilization/combustion area of DRI thermal/optical reflectance carbon analyser (plan view). In the most recent units the elbow between the volatilization/combustion zone and the MnO_2 oxidation zone has been eliminated; this eliminates the dead space in the flow, and also eliminates the cooler region between zones where condensation could occur.

heating, monitors the temperatures, FID output and reflectance, and integrates the FID response over the pre-specified temperature, oxidation and reflectance conditions.

An example of the DRI TOR carbon thermogram is shown in Fig. 4. In its current configuration total carbon is divided into seven carbon fractions as a function of temperature and oxidation environment. The TOR temperature in a pure He atmosphere ramps as rapidly as possible from ~ 25 to $120°C$ (OC1), 120 to $250°C$ (OC2), 250 to $450°C$ (OC3) and 450 to $550°C$ (OC4). Ramping to the next temperature or atmosphere begins when the FID response returns to baseline or a constant value—subject to the condition that the time spent in any segment (OC1, OC2, etc.) never be less than 80 s nor more than 580 s (no more than 850 s, in the case of EC1). When this condition has been reached in the OC4 segment, the 2% O_2/98% He atmosphere is introduced and peaks are integrated at $550°C$ (EC1), $700°C$ (EC2) and $800°C$ (EC3) until in each case the FID response returns to baseline or zero slope.

Figure 4 also shows the fraction of pyrolysed organic carbon which is detected in the O_2/He atmosphere at $550°C$ prior to the return of reflectance to its original value. The optical pyrolysis correction assumes that the light extinction per unit mass of pyrolytically produced carbon is the same as the light extinction per unit mass of carbon removed after turning on the O_2 until reflectance returns to its original value. A delay of approximately 25 s is shown in Fig. 4 between the time the O_2/He atmosphere is introduced and the EC1 segment of the FID output begins. Similarly there is an equal delay of approximately 25 s between the time the reflectance attains its original value and the end of the FID integration interval. This delay is the time it takes for the gaseous carbon to reach the FID. This delay is a constant for each instrument, and it is determined from the time difference between a rise in temperature and the FID response to potassium hydrogen phthalate (KHP) and sucrose standards. Each of these seven integrals is reported separately, as is the fraction which constitutes the pyrolysis correction and the standard TOR definitions of organic and elemental carbon.

The FID response is ratioed to a reference level of CH_4 injected at the end of each sample analysis cycle. Performance tests of instrument calibration are conducted at the beginning and end of daily operations (injections of CO_2 and CH_4 standards), as well as at
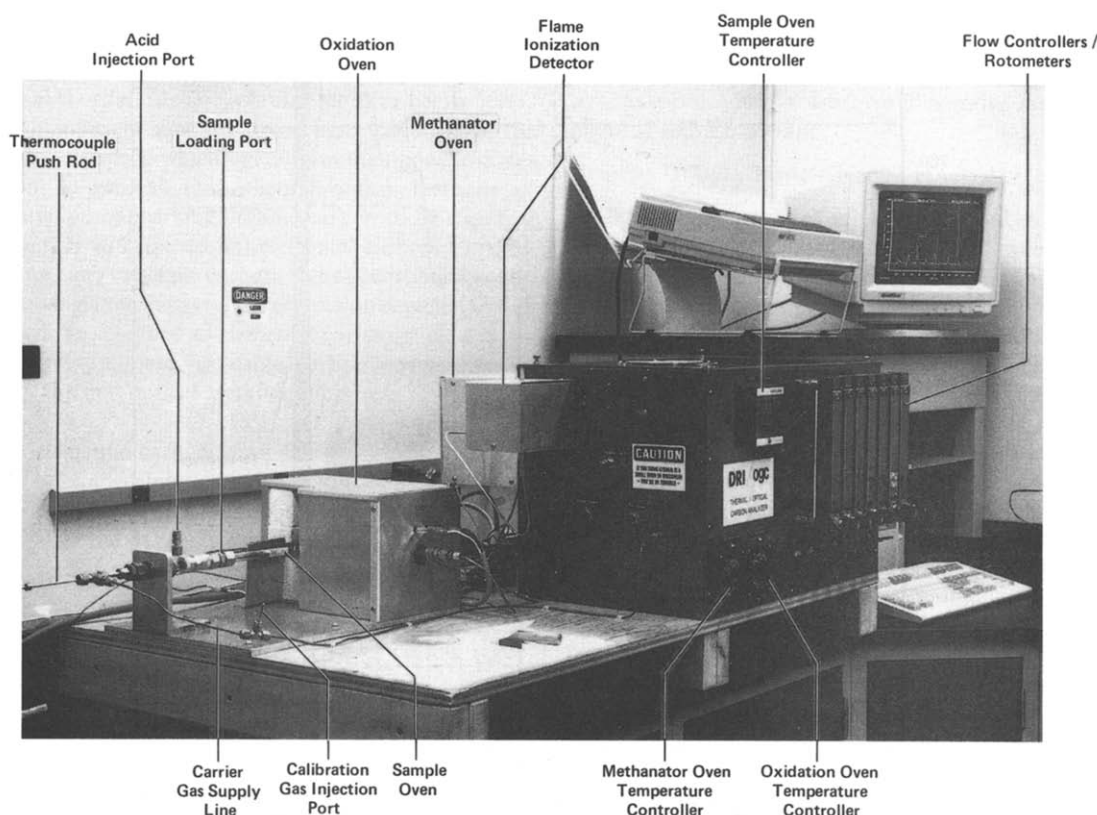
Fig. 3. Carbon analysis hardware.

the end of each sample run (integration of CH_4 reference peak, Fig. 4). All intervening samples are re-analysed if the calibration changes by more than 5%. Table 1 summarizes the precision and accuracy of the TOR system. Detailed carbon analysis procedures can be found in the DRI standard operating procedure (Pritchett et al., 1990).

The system is calibrated every 6 months by analysing samples of known amounts of CH_4, CO_2, sucrose and KHP. Shifts between calibrations are found to be only around 1–3%. American Chemical Society (ACS) certified reagent-grade crystal sucrose and KHP are burned as verification of the organic carbon fractions. Realistic ambient aerosol standards for organic and elemental carbon and to validate the organic/elemental carbon split are still lacking.

One of the greatest concerns in thermal or thermal/optical carbon analysis is to be sure that trace O_2 is not present during the organic carbon part of the analysis—from leaks, inadequate He purification, or any other cause. Trace O_2, if present, will cause organic carbon to be overestimated and elemental carbon correspondingly underestimated. To check on this, the FID signal approaching the end of OC4 is monitored for any continuing downward drift that would signify the presence of trace O_2. It has been suggested (S. H. Cadle, 1992, pers. commun.) that filters very lightly loaded with carbon black could be run from time to time as a further check for trace O_2.

Central to the optical pyrolysis-correction concept is the presumption, stated above, that the light absorption per unit mass of pyrolytically produced carbon is equal to the light absorption per unit mass of carbon burned in restoring the reflectance to its initial value (i.e. that the amount of carbon pyrolysed in creating the reflectance decrease and the amount of carbon burned in canceling the decrease are the same). There is no fundamental reason why they have to be exactly the same; and indeed they may not be (see comparison between photoacoustic and thermal/optical/extraction measurements below). Accordingly, there can be a residual bias in the demarcation between light-absorbing and non-light-absorbing carbon. This bias can be in either direction, in principle, resulting in under-correction or overcorrection for pyrolysis. The bias would appear largest when stated as a percentage of organic carbon, or elemental carbon, in cases where the other species predominates. Usually organic carbon is the more abundant, so the percentage effect is more significant for the elemental carbon. To date there are no estimates of possible magnitudes of such biases, but of course they would be smaller than the error of having no optical correction at all.

Another optical effect to be considered is that of light-absorbing organic carbon. If volatilizable, it should manifest itself in the thermogram by an increase in reflectance before the O_2 is switched on. Such increases are occasionally observed, but generally only
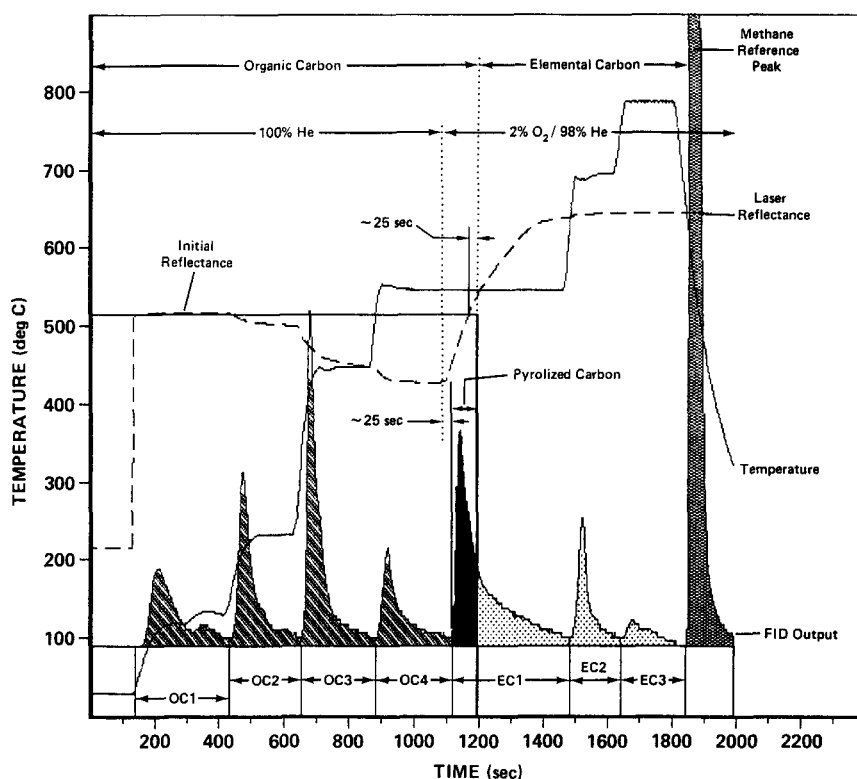
Fig. 4. Example of DRI thermal/optical reflectance carbon analyser thermogram. Reflectance and FID output are in relative units. Reflectance is normalized to initial reflectance and FID output is normalized to the area of the reference peak. This is an ambient sample collected on 17 May 1989 in Yellowstone National Park.

Table 1. Specifications of the DRI thermal/optical reflectance carbon analyser

Subject	Specification
Sample requirements	Substrate: quartz-fiber filter, Pallflex 2500QAT-UP or equivalent
	Substrate pretreatment: pre-fired at 900°C for at least 3 h (before sampling)
	Sample size: 0.5 cm² punch (uniform deposit)
	Sample storage: store below 4°C
Analysis time	880–4890 s (15–82 min)
Measurement range	0.2–750 μg carbon cm^{-2}
Detection limit	0.2 μg carbon cm^{-2}
FID precision	0.1% of full scale
Reflectance signal precision	0.2% of full scale
Sample oven temperature precision	$\pm 10°C$ at temperatures $<450°C$
	$\pm 3°C$ at temperatures $\geqslant 450°C$
Oxidation oven temperature	$912 \pm 5°C$
Methanator oven temperature	$550 \pm 5°C$
Lower quantifiable limits	Organic carbon: 0.5–1.0 μg carbon cm^{-2}
	Elemental carbon: 0.0–0.2 μg carbon cm^{-2}
	Carbonate carbon: 0.0–0.4 μg carbon cm^{-2}
Total carbon accuracy	$\pm 5\%$
Total carbon precision	For sample loading <10 μg carbon cm^{-2}: $\pm 0.5\mu$g carbon cm^{-2}
	For sample loading $\geqslant 10$ μg carbon cm^{-2}: $\pm 3\%$
OC/EC split precision	5% of the total carbon measurement
OC/EC split accuracy	To be determined*

* Probably 10% of the total carbon, by inference from the similar OGI instrument (Johnson et al., 1981).

in soil (not aerosol) samples where it is suspected that internal oxidant is involved. This common absence of increase implies that any light-absorbing organic material is ordinarily not volatilizable at or below 550°C in a sufficient amount to be observable above the pyrolysis effect, which operates in the opposite direction. In general, then, thermal/optical methods all cause light-absorbing organic carbon to be classified together with (hence, as) elemental carbon. Furthermore, any organic carbon, light-absorbing or not, evolving after the pyrolysis correction depicted in Fig. 4 will be classified as elemental carbon.

To recapitulate, "elemental carbon" as measured by any thermal/optical method comprises:

(1) elemental carbon,
(2) light-absorbing organic carbon,
(3) organic carbon, light-absorbing or not, evolving after the pyrolysis correction,
(4) bias, in either direction, in the pyrolysis correction.

Another interference we have seen is a color change by certain non-carbon species, which affects reflectance; fortunately, this is very rare.

Total carbon (commonly designated as TC) is the sum of organic carbon (OC), elemental carbon (EC) and carbonate carbon (e.g. Na_2CO_3, $MgCO_3$, K_2CO_3, $CaCO_3$). Carbonate carbon can be determined by measuring the CO_2 evolved upon acidification of the sample punch before the normal carbon analysis cycle. For carbonate determination, a 25 μl microsyringe is used to inject 20 μl of 0.4 M hydrochloric acid onto the filter punch via the injection port. The sample oven is maintained at ambient temperature while the heating coil (Fig. 2) is off, and the evolved CO_2 is measured as CH_4 by the FID in a 2% O_2/98% He atmosphere. The sample punch is dried at 40°C after the FID output returns to baseline prior to commencing the routine carbon analysis.

The carbonate procedure is usually not applied in carbon analysis, since carbonate carbon has been found to constitute less than 5% of the total carbon in most samples. Without acidification, carbonate carbon is detected as either organic or elemental carbon. According to their listed decomposition temperatures, carbonates could evolve in almost any region of the thermogram (e.g. $CaCO_3$, aragonite, 825°C). Novakov and colleagues (Novakov, 1981, 1982; Rosen et al., 1982) state that carbonate in their ambient aerosol samples evolved mainly at ~600°C, which would put it in the EC2 region of Fig. 4. Thus, even if carbonate amounts to less than 5% of the total carbon it can represent a substantial percentage of apparent elemental carbon if not removed first by acidification. This should always be considered in deciding whether or not to dispense with the carbonate procedure on a given type of sample. The carbonate blank introduced by absorption of ambient CO_2 onto the quartz-fiber filter also deserves consideration, especially since pre-firing the filter probably creates alkaline surface sites.

Salts of volatile organic acids, if present, will contribute to the carbonate reading and will be correspondingly missing from the organic analysis if the carbonate procedure is used. An illustrative example might be sodium acetate:

$$HCl(g) + NaAc \rightarrow NaCl + HAc(g)\uparrow.$$
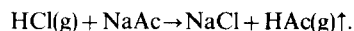
Thus "carbonate carbon" might be referred to more properly as "acid-released carbon" and, when the carbonate procedure is used, one should be aware of the potential effect on organic carbon.

All carbon measurements performed at DRI since mid-1987 have been made using these procedures. The intent of the temperature/atmosphere steps is to provide carbon fractions which are comparable to the operational definitions of "organic carbon" and "elemental carbon" derived from other analysis methods. It was found, in the course of this work, that the thermograms from source samples were substantially different between one source type and another (Watson et al., 1991a), in that the distribution among the seven fractions was distinctive of each source type. These carbon fingerprints appear to hold promise for separating sources such as wood stoves, fireplaces, diesel-powered vehicles and gasoline-powered vehicles from each other using receptor models.

COMPARISON WITH OTHER METHODS

The major area of concern in thermal carbon analysis is that there is at present no common definition of organic or elemental carbon.* Each of the thermal carbon analysis methods divides the evolved carbon into segments which are defined by: (1) temperature, (2) rate of temperature increase, (3) composition of atmosphere surrounding the sample and (4) method of optical correction for pyrolysis.

The definitions of organic and elemental carbon are, therefore, operational and reflect the method and purpose of measurement. For light extinction budgets, light-absorbing carbon is a more useful concept than elemental carbon. Light-absorbing carbon is not entirely constituted by graphitic carbon, since there are many tarry organic materials which absorb light. Even the "graphitic" black carbon in the atmosphere has only a poorly developed graphitic structure with abundant surface chemical groups such as hydroxyl. For source apportionment by receptor models, one would want to have several distinct fractions of carbon in both source and receptor samples. Differences in ratios of the carbon concentrations in

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* The ambiguity in the definitions of organic and elemental carbon is conceptual as well as practical. For example, in the homologous series of polynuclear aromatic hydrocarbons, as carbon/hydrogen ratio approaches infinity the content in the distinction between organic and elemental carbon gradually disappears. On the other hand, operational definitions notwithstanding, any acceptable method must read sucrose as 100% organic carbon and ultrapure graphite as 100% elemental carbon.

these fractions form part of the source profile which distinguishes the contribution of one source from the contributions of other sources (Watson et al., 1991a).

The comparisons discussed here comprise several variations of the thermal (T), thermal/optical reflectance (TOR), thermal/optical transmission (TOT) and thermal manganese oxidation (TMO) methods for organic and elemental carbon; spiking experiments for elemental carbon; and elemental carbon by optical absorption (OA), photoacoustic spectroscopy and nonextractable mass. The thermal (T) methods, as distinct from thermal/optical methods (TOR, TOT), have no optical correction for pyrolysis. The TOT method (Sunset Laboratory, 1990; Turpin et al., 1990a) differs from TOR in that it uses transmission instead of reflectance for the optical pyrolysis correction. The TMO method (Mueller et al., 1982; Fung, 1990) uses MnO_2, present and in contact with the sample throughout the analysis, as the oxidizing agent, and temperature is relied upon to distinguish between organic and elemental carbon; carbon evolving at 525°C is classified as organic carbon, and carbon evolving at 850°C is classified as elemental carbon.

All of the carbon analysis methods—T, TOR, TOT, TMO—agree within 5–15% on the sum of organic and elemental carbon in ambient samples and source samples (Countess, 1990; Houck et al., 1989b; Kusko et al., 1989; Shah and Rau, 1991) and, on average, within 3% in standard samples (see Table 2). Evaluation of these methods then becomes a matter of assessing how they differentiate between organic and elemental carbon. Comparison with respect to elemental carbon alone is a convenient way to compare methods since organic carbon is essentially the complement of elemental carbon.

The TOR systems at OGI and DRI give similar splits between organic and elemental carbon (Countess, 1990; Shah and Rau, 1991), within ~12% referred to elemental carbon or a few per cent referred to total carbon. This result is from the Carbonaceous Species Methods Comparison Study (CSMCS; Hering et al., 1990; Lawson and Hering, 1990), conducted by the California Air Resources Board. In the CSMCS several variations of the T, TOR, TOT, TMO and OA methods were applied to ambient samples including samples from woodburning-dominated environments, source samples from diesel and various types of spark-ignition vehicles and a photolytic smog-chamber aerosol (Cadle and Mulawa, 1990; Countess, 1990; Fung, 1990; Shah and Rau, 1991; Turpin et al., 1990a).

Excellent agreement between OGI TOR elemental carbon and nonextractable (in toluene/n-propanol) mass has been obtained on diesel exhaust particulate matter (Japar et al., 1984a):

$$TOR/(nonextractable\ mass) = 1.05 \pm 0.04,$$

$$r = 0.93(n = 28).$$

Elemental carbon by DRI TOR is said (G. A. Allen, 1991, pers. commun.) to agree fairly well with real-time optical transmission measurements on the Lawrence Berkeley Laboratory aethalometer (Hansen et al., 1982) in the Harvard Uniontown, PA, Acidic Aerosol Study in July and August 1990:

$$aethalometer/TOR = 0.89 \pm 0.04,$$

$$r = 0.93(n = 72).$$

Table 2 summarizes recent laboratory audits as part of the SCENIC Denver Study (Watson et al., 1988b). These performance audits were conducted by ENSR Consulting and Engineering Inc. (Collins, 1988; Gertler et al., 1988) to test the accuracy and precision of the DRI TOR analysis. Aqueous solutions of KHP and methanol suspensions of graphite, the latter supposedly submicron in size (C. E. McDade, 1991, pers. commun.), were deposited in stated amounts onto the centers of pre-fired filters using a microsyringe (accuracy $\pm 0.54\%$). This resulted in a dense inhomogeneous deposit. As shown in Table 2, the elemental carbon values reported by the DRI TOR method were 1–2 $\mu g\ cm^{-2}$ higher than the values from gravimetric analysis (weight difference of the filter before and after deposition of the graphite). This error represents 28–40% of the elemental carbon but only 2–5% of the total carbon, and some of it may be in the gravimetric determination. Organic carbon results appear reasonable, showing an average difference of 7% from the amount present. Overall, DRI TOR analyses resulted in lower-than-stated organic carbon and higher-than-stated elemental carbon, indicating the possibility that some organic carbon was misclassified as elemental carbon, though the error is small (~5%) relative to total carbon. The biggest problem was that the sample deposit area was smaller than the area of the laser beam so that the laser signal-to-noise ratio was poor.

There is good agreement between TOR and TOT in some studies but not in all. In the CSMCS ambient samples, collected in the Los Angeles Air Basin at Citrus College in Glendora, CA, the elemental carbon averages stood in the order TOR > OA > TMO ≈ T > TOT. The difference in elemental carbon between TOR and TOT was roughly a factor of two; elemental carbon constituted ~20% of the carbon in these samples, so the disparity corresponds to ~14% of the total carbon. In the CSMCS source samples, TOR and TOT agreed within ~1% on diesel exhaust particulate matter (elemental carbon ≈ 80% of total carbon) but TOR exceeded TOT on the others, the worst being the woodsmoke-dominated samples where the disparity was four- to seven-fold in elemental carbon. Houck et al. (1989b) found disparities in comparisons of nine different types of source samples and source-dominated samples, and reported elemental carbon ratios $\overline{TOR/TMO/TOT} \simeq 1.6/1.35/1$; the comparison is discussed in more detail by Shah and Rau (1991).

Table 2. Summary of performance audits with laboratory spiked samples

I. Laboratory audits as part of the SCENIC Denver study (Collins, 1988) using mixtures of KHP and graphite; see text

	Organic carbon from KHP				Elemental carbon from graphite				Total carbon			
ENSR spike (μg cm^{-2})	DRI (μg cm^{-2})*		Absolute difference		ENSR spike (μg cm^{-2})	DRI (μg cm^{-2})*		Absolute difference	ENSR spike (μg cm^{-2})	DRI (μg cm^{-2})*		Absolute difference
			μg cm^{-2}	Per cent†				μg cm^{-2}	Per cent			μg cm^{-2}	Per cent
(Blank)	1.74±0.56				(Blank)	0.14±0.15			(Blank)	1.88±0.59		
17.89	16.81±0.53‡§		-1.08	-6	2.47	3.44±0.42‡§		0.98	40	20.36	20.25±0.94‡§	-0.11	-1
53.68	48.42±7.05‡§		-5.26	-10	7.4	9.44±0.76‡§		2.04	28	61.08	57.86±6.72‡§	-3.22	-5
71.57	68.67±0.85‡§		-2.90	-4	3.7	4.87±1.20‡§		1.18	32	75.27	73.55±0.72‡§	-1.72	-2

II. Interlaboratory comparison as part of the Phoenix and Tucson Urban Haze and PM10 studies (Tomlin and McDade, 1991)

Organic carbon from KHP

ENSR spike	DRI (μg punch^{-1})*	Sunset (μg punch^{-1})*	Absolute difference (DRI minus Sunset) μg punch^{-1}	Per cent||
(Blank)	1.6±0.36	2.5±0.37	-0.9±0.52	-22
9	11.1±0.21‡	10.9±0.85‡	0.2±0.88	2
18	20.4±0.44‡	21.1±0.10‡	-0.7±0.45	-3
36	37.9±1.01‡	38.3±2.00‡	-0.4±2.24	-1

* Three samples were performed per set.
† DRI minus ENSR spike, divided by ENSR spike.
‡ Blank corrected.
§ Colored residue left on filter.
|| DRI minus Sunset, divided by their average.

Agreement in the 1–3% range between TOR at DRI and TOT at Sunset Laboratory was reported by Tomlin and McDade (1991) in KHP spiking experiments conducted as part of the Phoenix and Tucson Urban Haze and PM10 Studies (Chow et al., 1991a,b; Watson et al., 1991b,c), as shown in Table 2; but the significance is limited in that KHP is by no means a severe challenge. Both laboratories read ~ 2 μg per punch higher than the spiked KHP standard.

To resolve the difference between TOR and TOT, a fourth-generation thermal/optical reflectance/transmittance carbon analyser has been developed by DRI for the South Coast Air Quality Management District (SCAQMD; Pritchett et al., 1991a,b). This unit possesses all of the features of the third-generation system, plus:

• concurrent reflectance and transmittance measurements, allowing direct comparison between TOR and TOT on the same sample,
• particle light absorption (b_{abs}) measurements by transmittance on each of the carbon fractions,
• automatic sample insertion, enhancing sample-position reproducibility and increasing the precision of the laser reflectance and transmittance measurements from sample to sample,
• modified sample processing module, to accommodate additional features such as a chromatographic column downstream of the oven heating coil for identifying individual species in the thermogram,
• improvements in ruggedness, ease of maintenance and repair, ease and efficiency of operation, software versatility and other practical features.

Initial testing demonstrated comparable results between the third and fourth generations of carbon analysers on homogeneously deposited samples. Reflectance and transmittance measurements on 15 ambient samples with the fourth-generation analyser then resulted in equivalent laser demarcations ($\pm 5\%$ referred to total carbon) between organic and elemental carbon, indicating that the TOR and TOT methods were equivalent on these samples.

Shah and Rau (1991) have suggested that in the TOR and TOT methods the reflectance of the filter surface regains its initial value before the transmittance does, because of unburned pyrolytic material beneath the surface, causing TOR to be undercorrected for pyrolysis and hence to read erroneously high on elemental carbon while TOT is more nearly correct. Countess (1990) concludes that TOR underestimates the amount of charring compared to TOT, and support can be found in certain observations by Turpin et al. (1990a) regarding filter blackening. On the other hand, TOR and TOT gave similar results when applied in the same instrument; in such a case hypotheses to rationalize differences, even if the hypothesized processes occur, are unnecessary. Many more comparisons of TOR and TOT must be made to see whether or not they are equivalent.

If TOR and TOT are equivalent, then TOR can be evaluated further through evaluation of TOT. Comparison of the TOT method (two laboratories) with photoacoustic spectroscopy gave excellent agreement on elemental carbon. This was established on Dearborn, MI, ambient aerosol in 1986 (Adams et al., 1989) and on Claremont, CA, ambient aerosol in 1987 during the Southern California Air Quality Study (SCAQS; Adams et al., 1990a; Turpin et al., 1990b). In some of the comparisons, samples for TOT analysis were first extracted with toluene/n-propanol to remove most of the organic carbon and thereby to reduce the pyrolysis correction. Regression analysis gave an insignificant zero intercept in all comparisons, with slopes and correlation coefficients as follows:

(1) Without extraction:

Photoacoustic/TOT $= 0.92 \pm 0.06$,

$r = 0.905 (n = 59)$,

Claremont (Turpin et al., 1990b)

Photoacoustic/TOT $= 1.08 \pm 0.10$,

$r = 0.914 (n = 41)$,

Claremont (Adams et al., 1990a).

(2) With extraction:

Photoacoustic/TOT $= 1.10 \pm 0.13$,

$r = 0.926 (n = 14)$,

Dearborn (Adams et al., 1989)

Photoacoustic/TOT $= 1.006 \pm 0.056$,

$r = 0.945 (n = 26)$,

Claremont (Adams et al., 1990a).

This improved agreement concomitant to extraction in the Claremont experiment by Adams et al. (1990a) should be noted. Adams et al. (1990a) surmise that in the TOT procedure there is a systematic overcorrection for pyrolysis, and that the improvement effected by extraction results from removal of material capable of pyrolysing. (Note that extractable light-absorbing organic carbon would act in the opposite direction.) The authors state, "Since the two measurement techniques, photoacoustic spectroscopy and thermal/extraction, are based on entirely different principles, their excellent agreement provides strong evidence for the validity of both experimental methods for the measurement of atmospheric EC aerosol."

Note that the putative overcorrection for pyrolysis in TOT and the earlier-hypothesized undercorrection in TOR would together be consistent with elemental carbon reading higher by TOR than by TOT if such a difference does exist. All of this ignores the slope 0.92 result from Turpin et al. (1990b) above, which would be consistent with undercorrection for pyrolysis in TOT.

TOR and TMO agreed within a few per cent in elemental carbon in the diesel exhaust particulate sample from the CSMCS. Elemental carbon in the

smog-chamber aerosol read ~2% of total carbon by TOR/TOT, 8% by TMO, and presumably was in fact zero. Otherwise, TOR was consistently higher than TMO on elemental carbon, more so when elemental carbon was a small fraction of total carbon. In the ambient samples (elemental carbon ≃20% of total carbon), the disparity was a factor of 1.6 ± 1.2, or ~9% of the total carbon. The worst disparity was in the two woodsmoke-dominated samples (elemental carbon ≃11% of total carbon), with TOR/TMO ratios 8 and 53—and with TMO lower by far than any other method (T, TOR, TOT, OA). TMO in one sample gave only 25% as much elemental carbon as the mean of the other methods and laboratories; and in the other sample, TMO gave only 4% as much.

Differences between the TOR and TMO methods were again observed during the 1987 WHITEX study (Malm et al., 1989) when the IMPROVE (Eldred et al., 1988, 1989, 1990) and SCISAS (Mueller et al., 1986; Rogers et al., 1989) samplers were collocated in Page, AZ, to obtain PM2.5 aerosol on some 60 pairs of pre-fired quartz-fiber filters. IMPROVE samples were analysed at DRI using the TOR method and the SCISAS samples were analysed at ENSR Consulting and Engineering Inc. using the TMO method. Though the total carbon concentrations were comparable (Kusko et al., 1989), the elemental carbon concentrations measured by TOR were five or six times the elemental carbon levels by TMO and the correlation was only modest ($r = 0.84$; Shah, 1988). These were samples in which elemental carbon constituted ~35% of the total carbon on average according to TOR, or 10% according to TMO. The wintertime samples at Page were said to contain large contributions from wood smoke (Shah, 1988). When the thermograms from the IMPROVE/TOR samples were examined, it was concluded that the elemental carbon fraction which evolved at 800°C was mostly the same material as the elemental carbon measured at 850°C by the SCISAS/TMO method.

TOR read lower than TMO on elemental carbon as often as not, with an average ratio $(TOR/TMO)_{ave} = 0.94 \pm 0.88$, in the comparison by Houck et al. (1989b) of 20 source samples and source-dominated samples (soil, road dust, fireplace, wood stove, diesel bus, field burning, construction dust, dairy dust and crude-oil-burning emissions; see also Shah and Rau, 1991). The range of concentrations in these samples was extremely broad ($>100 \times$). The regression was:

$$TMO = 0.900 \, TOR - 0.056, \quad r = 0.971 (n = 20).$$

(The dimensions of the intercept term are $\mu g \, cm^{-2}$ of filter.) In addition, TOR organic carbon was higher than TMO organic carbon in 15 of the 20 samples. These results, given the strong correlation and the near-zero intercept and the data quality that this suggests, appear to bring into question the other TOR vs TMO comparisons.

A comparison was attempted between TOR and TMO elemental carbon in the SCENIC Denver labor-
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atory audits on the KHP and graphite spiking experiments (Collins, 1988; Gertler et al., 1988). But Collins (1988) reported difficulty in obtaining TMO elemental carbon values owing to incomplete combustion of the carbon punch.

It is unclear, then, whether TOR is higher than TMO on elemental carbon or not. It is easy to imagine, however, why TOR should be higher than TMO on elemental carbon:

(1) The TOR optical correction may be under-correcting for pyrolysis as discussed above. Also, TOR classifies as elemental carbon all light-absorbing carbon, and all organic carbon evolving in the region whether light-absorbing or not (e.g. organic carbon requiring O_2 attack in order to evolve).

(2) The entire EC1 area in Fig. 4 would probably be classified as organic carbon by the TMO method, since the TMO method classifies as organic carbon all carbon evolved at 525°C in the presence of oxidant, similar to the conditions for EC1, namely, 550°C and 2% O_2. Since EC1 sometimes contains much of the light-absorbing carbon (nearly all, in the example illustrated in Fig. 4), misclassification could be of great consequence. Without knowing what the material is (e.g. elemental carbon, non-volatile organic material, undercorrected pyrolytic material), one cannot tell which method, if either, is classifying it correctly. An important point, however, is that, at the 550°C at which it evolved in 2% O_2, it did not evolve earlier when O_2 was absent (i.e. it did not evolve in OC4). Elemental carbon is reported to be oxidizable at temperatures as low as 400°C (Shah and Rau, 1991; O_2 partial pressures not stated) or, in air, even 350°C (Cadle and Mulawa, 1990)—though rates are not stated in either report. Light-absorbing carbon, stated to be mostly graphitic in nature, is evolved from ambient and source samples at temperatures as low as 440–470°C in pure O_2 (Novakov, 1981, 1982; Rosen et al., 1982) and as low as 400–550°C in air (Rosen et al., 1977, 1979). Oxidation of elemental carbon during thermal analysis of aerosol filter samples in an air stream, in the presence of trace catalytic substances from the filter or in the sample itself, has been documented by Lin and Friedlander (1988a,b,c) at temperatures well below 500°C. Accordingly it seems likely that the TMO method must misclassify at least some elemental carbon as organic carbon; that is, at least some of the EC1 area is misclassified as organic by the TMO method. (It follows that oxidizing substances, if present, within the sample itself, could cause evolution of elemental carbon even before the O_2 is switched on in the thermal or thermal/optical methods.)

(3) The "lighter-fluid effect", as it is known in automotive programs on regenerative particulate traps, wherein elemental carbon is ignited through combustion of organic carbon, would cause elemental carbon to be misclassified as organic carbon by the TMO method.

Of these processes, the first would cause TOR elemental carbon to be high, the second could cause

errors in either direction but probably would cause TMO elemental carbon to be low, and the third would cause TMO elemental carbon to be low.

Another factor that should be considered is that the TMO analytical conditions are derived based on properties of polycrystalline graphite as the elemental carbon. High-molecular-weight material that is virtually elemental carbon in composition, or in general forms of "elemental carbon" less difficult to oxidize than polycrystalline graphite, will be classified as organic by the TMO method as presently calibrated.

The excellent agreement among TOR, TMO and TOT—and between TOR and nonextractable mass — on diesel exhaust particulate matter is informative when set against the situation on wood-smoke-dominated samples. There is very little polymeric or light-absorbing organic material in diesel exhaust particulate matter (Szkarlat and Japar, 1983). Most of the light-absorbing carbon exhibits a weakly ordered structure approaching that of polycrystalline graphite (Rosen and Novakov, 1977; Rosen et al., 1978, 1979, 1982). For chemical reactivity purposes this structural description may be misleading. It is more appropriate to think of the material as consisting of assemblies of large (~ 130 carbon atoms) stacked polynuclear aromatic hydrocarbon molecules of dimensions $\sim 2 \times 2$ nm, six layers per stack, with reactive chemical groups on many or most of the edge carbons (Ebert, 1990). Possibly this material would evolve at high enough temperatures to be classified as elemental carbon by all methods, whereas some of the light-absorbing carbon in woodsmoke-dominated samples may evolve under conditions ($525°C$ in the presence of oxidant) which in the TMO method would classify it as organic but which in the TOR method would classify it as elemental. Also, pyrolysis should be relatively unimportant in diesel exhaust particulate matter. In fact, the TOR thermogram of diesel exhaust particulate matter exhibits very little EC1 and is almost devoid of optical evidence of pyrolysis and hence of pyrolytic material or pyrolysis correction (Watson et al., 1991a). Indeed, Japar et al. (1984a) report a pyrolysis correction amounting to only $3 \pm 3\%$ of the total carbon. Thus we are led again to focus on the EC1 region and on the pyrolysis correction as holding the key(s) to the differences among the various methods.

A good way to visualize part of what might be happening is to consider vulcanized rubber. Vulcanization creates crosslinks among polymer chains, after which the material is insoluble in organic solvents except under high-temperature (e.g. 180°C) oxidative attack to break the crosslinks. Fraction EC1 may well contain analogous substances which, though light-absorbing and not removable except through oxidation at elevated temperature, are not elemental carbon in any sense (vulcanized rubber copolymer has hydrogen/carbon atom ratio $\simeq 1.5$). There is a need to explore carefully the behavior of polymeric material (e.g. cellulose) in the various carbon analytical procedures

APPLICATIONS OF THE TOR METHOD

Over 27,000 ambient and source samples have been analysed with the third-generation TOR carbon analysers since mid-1987. Table 3 summarizes the major visibility, PM10 State Implementation Plan development, source characterization and special air quality studies in which the DRI TOR method described above has been applied.

SUMMARY AND RECOMMENDATIONS

The thermal/optical reflectance (TOR) method of carbon analysis has been applied to quantify organic and elemental carbon on source and receptor samples collected in most large-scale air quality studies conducted in the U.S.A. This paper states the history and evolution of the TOR method over the past decade. The key factors governing different carbon analysis methods are: (1) temperature setting, (2) rate of temperature increase, (3) composition of atmosphere surrounding the sample, (4) method of optical correction for pyrolysis and (5) standardization. Efforts have been made on both hardware and software of the carbon system to refine the temperature programming, to report multiple carbon fractions and to compare the reflectance and transmittance optical correction for pyrolysis.

The major air quality studies in which the TOR method has been applied are identified. Comparison to other methods and to other variations of the TOR method are summarized. It is often stated that the various carbon analysis methods do not agree. The actual situation is worse than that: there is not even agreement on what the disagreements are. Research is needed in the following areas:

- Evaluate the various methods, with and without sample pre-extraction, against photoacoustic spectroscopy or other primary method for elemental carbon. Do so for a variety of sample types, including high-polymer materials and samples in which organic carbon predominates over elemental carbon.
- Directly compare TOR vs TOT. Evaluate the assumptions underlying the optical pyrolysis correction in each method. Employ more extensive and more diverse sample sets than were utilized above.
- Develop realistic aerosol organic, elemental and mixed organic/elemental carbon standards.
- Identify, by GC/MS and/or other means, the individual chemical species constituting the different carbon fractions (currently seven, in the DRI TOR procedure) of the various methods, especially the fractions adjacent to the division between organic and elemental carbon.

At some point further intercomparisons among methods and laboratories may be warranted, but at present they are unlikely to produce anything definitive.

Table 3. Summary of DRI thermal/optical reflectance carbon analysis applied in major air quality studies in the U.S.A.

I. Visibility studies

Winter Haze Intensive Tracer EXperiment (WHITEX; Malm et al., 1989, 1990; Mathai, 1990)

Interagency Monitoring of PROtected Visual Environments (IMPROVE; Joseph et al., 1987; Eldred et al., 1988, 1989, 1990)

NorthEast States for Coordinated Air Use Management (NESCAUM; Poirot and Di Genova, 1990; Flocchini et al., 1990)

Pacific northwest REgional Visibility experiment with Natural Tracers (PREVENT; R. A. Eldred, 1991, pers. commun.)

The 1987–88 Metro Denver Brown Cloud Study (Watson et al., 1988a,b,c; Mathai, 1990)

The 1989–90 Phoenix Urban Haze Study (Watson et al., 1990a, 1991b)

The 1989–90 Pilot Tucson Urban Haze Study (Watson et al., 1990b, 1991c)

II. PM10 SIP development

State of Nevada Air Pollution Study (SNAPS; Chow et al., 1986, 1988, 1989a; Watson et al., 1988d; Benedict and Naylor, 1988)

Rubidoux, CA, Neighborhood-scale PM10 Study (Chow et al., 1989b,c,d, 1992a)

Valley Air Quality Study (VAQS; Chan et al., 1990; Chow et al., 1990a, 1992b, 1993)

Santa Barbara PM10 Study (Countess, 1991)

The 1989–90 Phoenix PM10 Study (Watson et al., 1990c; Chow et al., 1991a)

The 1989–90 Pilot Tucson PM10 Study (Watson et al., 1990d; Chow et al., 1991b)

Development of other PM10 SIPs (Chow et al., 1990b)

III. Special studies

San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures–Predictions and EXperiment (SJVAQS/AUSPEX) Aerosol and Visibility Study (Chow and Richards, 1990a,b)

Harvard Uniontown Acidic Aerosol Study (G. A. Allen, 1991, pers commun.)

IV. Source characterization studies

California Air Resources Board's Source Characterization Studies (Houck et al., 1989a–e; Ahuja et al., 1989)

Pacific Northwest Source Profile Library (Core and Houck, 1987; Core, 1989)

SNAPS Source Profile Development (Watson et al., 1988d)

Denver Source Profile Development (Watson et al., 1988b)

Phoenix Source Profile Development (Chow et al., 1991a)

Tucson Source Profile Development (Watson et al., 1990d; Chow et al., 1991b)

Santa Barbara Source Profile Development (Countess, 1991)

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