ELEMENTAL CARBON (DIESEL PARTICULATE) 5040

C	AW: 12.01	CAS: none	RTECS: none

METHOD: 5040: Issue 3 (Interim)	EVALUATION: FULL	Issue 1: 15 May 1996
		Issue 3: 30 September 1999 (Interim)

OSHA : no REL
NIOSH: no PEL
ACGIH: see APPENDIX A

PROPERTIES: nonvolatile solid; MP >350 EC

SYNONYMS (related terms): soot, black carbon, diesel emissions, diesel exhaust particles, diesel particulate matter

SAMPLING	MEASUREMENT
SAMPLER: FILTER (quartz fiber, 37-mm; size-selective sampler may be required, see APPENDIX B)	**TECHNIQUE:** EVOLVED GAS ANALYSIS (EGA) by thermal-optical analyzer
FLOW RATE: 2 to 4 L/min (see APPENDIX B)	**ANALYTE:** elemental carbon (EC)
VOL-MIN: 142 L @ 40 µg/m³ **-MAX:** 19 m³ (for filter load of ~ 90 µg/cm²)	**FILTER PUNCH SIZE:** 1.5 cm² (see APPENDIX C)
SHIPMENT: routine	**CALIBRATION:** methane injection [1]
SAMPLE STABILITY: stable	**RANGE:** 1 to 105 µg per filter portion (see EVALUATION OF METHOD)
BLANKS: 2 to 10 field blanks per set	**ESTIMATED LOD:** 0.3 µg per filter portion

ACCURACY

PRECISION ($\bar{p}_r$): 0.19 @ 1 µg C,
0.01 @ 10 to 72 µg C

RANGE STUDIED: 23 to 240 µg/m³ (see EVALUATION OF METHOD)

BIAS: none (see EVALUATION OF METHOD)

OVERALL PRECISION ($\ddot{O}_{rT}$): 0.085 at 23 µg/m³ (see EVALUATION OF METHOD)

ACCURACY: ± 16.7% at 23 µg/m³ (see EVALUATION OF METHOD)

APPLICABILITY: The working range is approximately 6 to 630 µg/m³, with an LOD of ~ 2 µg/m³ for a 960-L air sample collected on a 37-mm filter with a 1.5 cm² punch from the sample filter. If a lower LOD is desired, a larger sample volume and/or 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.4 µg/m³). The split between organic-based carbon (OC) and EC may be inaccurate if the sample transmittance is too low. The EC loading at which this occurs depends on laser intensity. In general, the OC-EC split may be inaccurate when EC loadings are above 20 µg/cm² of filter. High loadings can give low (and variable) EC results because the transmittance remains low and relatively constant until some of the EC is oxidized from the filter. The split should be reassigned (prior to EC peak) in such cases [1]. An upper EC limit of 800 µg/m³ (90 µg/cm²) can be determined.

INTERFERENCES: As defined by the thermal-optical method, EC is the carbon determined during the second stage of the analysis (after pyrolysis correction). If the sample contains no pyrolyzable material, all the carbon evolved during this stage is considered elemental. Cigarette smoke and carbonates ordinarily do not interfere, but if heavy loadings of carbonate are anticipated, a cyclone should be used (see APPENDIX B). For measurement of diesel-source EC in coal mines, an impactor with submicrometer cutpoint [2,3] must be used to minimize collection of coal dust.

OTHER METHODS: Other methods for determination of EC and OC have been described in the literature [4], but alternative instrumentation is currently not commercially available.

REAGENTS:

1. Aqueous organic-based carbon (OC) solutions (e.g., sucrose), 0.1 to 3 mg C per mL solution (ensure range brackets that for samples).
2. Helium, prepurified.
3. Hydrogen, purified.
4. Oxygen (10%) in helium, premixed, purified.
5. Methane (5%) in helium, premixed, purified.

EQUIPMENT:

1. Sampler: Quartz-fiber filter, precleaned (Clean in low temperature asher 2 to 3 h, or muffle furnace for 1 to 2 h at ~ 800 EC), 37-mm, in a 3-piece, 37-mm, cassette with support (stainless steel screen or cellulose pad). See also alternative samplers (APPENDIX B).
   NOTE: Cellulose supports give higher OC blanks than stainless.
2. Personal sampling pump, 2 to 4 L/min, with flexible tubing.
3. Thermal-optical analyzer (see APPENDIX C) or other analyzer capable of EC speciation.
4. Punch for removal of 1.5 cm^2 rectangular portion of filter.
   NOTE: Smaller portion may be taken (e.g., with cork borer), but portion $0.5 cm^2 with diameter or width # 1 cm is recommended.
5. Syringe, 10-µL.
6. Aluminum foil.
7. Needle (for lifting filter punch portion).

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: Open-faced cassettes give even deposits over the entire flow-rate range specified, but are not practical in some workplaces (e.g., mining). Alternative samplers also can be used (see APPENDIX B) provided that an even deposit of diesel particulate results. An even deposit is necessary because the sample portion analyzed must be representative of the entire deposit. If the deposit is not homogeneous, the entire sample must be analyzed.
2. Attach sampler outlet to personal sampling pump with flexible tubing. Remove top piece of cassette, unless sampling environment dictates otherwise (i.e., closed-face or other type sampler is required).
3. Sample at an accurately known flow rate (see APPENDIX B).
4. After sampling, replace top piece of cassette, if removed, and pack securely for shipment to laboratory.

SAMPLE PREPARATION:

5. Place sample filter on a freshly cleaned aluminum foil surface. Punch out a representative portion of the filter. Take care not to disturb deposited material and avoid hand contact with sample. A needle inserted at an angle is useful for removal of the filter portion from the punch body.

CALIBRATION AND QUALITY CONTROL:

6. Analyze at least one replicate sample. For sets of up to 50 samples, replicate 10% of the samples. For sets over 50 samples, replicate 5% of the samples. If a particular filter deposit appears uneven, take a duplicate portion (step 5) for analysis to check evenness of deposition.
   NOTE: Precision of replicate analyses of a filter is usually better than 5% (1 to 3% is typical).
7. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
   a. With 10-µL (or other) syringe, apply an aliquot of OC standard solution directly to filter portion taken

(step 5) from a precleaned filter. For best results, the precleaned filter punch should be cleaned again in the sample oven prior to application.

NOTE: With small aliquots (e.g., # 10 µL), disperse standard solution over one end of filter portion to ensure standard is in laser beam. To prevent possible solution loss to surface, hold the portion off the surface. Larger volumes can easily penetrate to the underside of the filter portion.

   b. Allow water to evaporate and analyze spikes with samples and blanks (steps 9 and 10).

NOTE: A decrease in filter transmittance during the first temperature step of the analysis indicates water loss. Allow portions to dry longer if this occurs.

8. Determine instrument blank (results of analysis with freshly cleaned filter portion) for each sample set.

MEASUREMENT:

9. Set analyzer according to manufacturer's recommendations (see APPENDIX C). Place sample portion into sample oven.

NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require a longer period and higher temperature during the 2nd part of the analysis to ensure that all EC is removed (the EC peak should never merge with the calibration peak). Adjust time and temperature accordingly. A maximum temperature above 940 EC should not be required.

10. Determine EC (and OC) mass, µg. Analyzer results are reported in units µg/cm^2 of C. The reported values are based on a sample portion of 1.5 cm^2, which is the area of the punch provided by the manufacturer. If the portion area differs from this value, multiply the reported result by 1.5 and divide the product by the actual area of the portion analyzed to obtain correct result (i.e., reported result x 1.5/actual punch area = corrected result in µg/cm^2).

CALCULATIONS:

11. Multiply the reported (or area-corrected) EC result (µg/cm^2) by filter *deposit area*, cm^2, (typically 8.55 cm^2 for a 37-mm filter) to calculate total mass, µg, of EC on each filter sample (W_{EC}). Do the same for the blanks and calculate the mass found in the average field blank (W_b).

12. Calculate EC concentration (C_{EC}) in the air volume sampled, V (L):

$$C_{EC} \cdot \frac{W_{EC} \ \& \ W_b}{V}, \ \text{mg/m}^3$$

EVALUATION OF METHOD:

Diesel exhaust is a chemically complex mixture containing thousands of compounds; therefore, some measure of exposure must be selected (See APPENDIX A). Rationale for selection of EC has been discussed elsewhere [1].

Because a suitable reference material is not available for determining the organic and elemental carbon content of a complex carbonaceous aerosol, only the accuracy of the method in the determination of total carbon (TC) could be examined. No discernable differences in the responses of five different organic compounds were noted. Linear regression of the data (43 analyses total) for all five compounds gave a slope and correlation coefficient (*r*) near unity [slope = 0.99 (± 0.01), r^2 = 0.999, *n* = 43]. Based on results for individual compounds, reported carbon values are expected to be from 98 to 100% of the actual amount present. In addition to the OC standards, eight different carbonaceous materials were analyzed by the thermal-optical method and the results were in good agreement with those reported by two other independent laboratories. These findings [1] indicate that instrumental response appears to be compound- and matrix-independent (i.e., carbon in a sample is accurately quantified irrespective of compound and matrix type). Such a response is required for accurate determination of carbon in samples of unknown composition.

To calculate the estimated limit of detection (LOD) of the method (i.e.,. 0.24 µg C, or 0.15 µg/cm^2),

ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to 2.82 µg C (or from 0.15 to 1.83 µg C per cm^2 of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e., µg C reported vs. actual) were then used to calculate the LOD as $3 s_y/\textbf{m}$ (where s_y is the standard error of the regression and **m** is the slope of the regression line). The calculated LOD shows good agreement with that estimated as LOD = $3s_{blank}$, which gives a value of . 0.3 µg C. The mean (n = 40) *instrumental* blank was 0.03 (± 0.1) µg C.

Like all OC-EC methods, the thermal-optical method is an *operational* method in the sense that the analytical procedure itself defines the analyte. Of the possible approaches for OC-EC analysis, this particular technique was investigated because it offers greater selectivity (pyrolysis correction) and flexibility (automated analysis, programmable parameter files) than previously used methods. The method is considered unbiased (i.e., it is the reference method), and the overall precision reflects method accuracy. The S_r of the mean EC concentration found with fourteen samplers (two each of seven types) for collection of diesel exhaust in a loading dock area where a diesel truck was operating was 5.6% [1]. Although pumps were used for sample collection, a 5% pump error was added in the calculation of the overall precision of the method because of the relatively small sample taken (0.5 h, 60 L). Based on the 95% confidence limit (19%; 13 degrees of freedom, n =14) on the accuracy, results of this experiment indicate that the NIOSH accuracy criterion [5] is fulfilled. The amount of EC collected (240 µg per sample) would be equivalent to sampling an EC level of 250 µg/m^3 for 8 h at 2 L/min.

In addition to this initial field test, laboratory-generated diesel particulate samples were analyzed. A dilution tunnel equipped with a dynamometer was used for generation of the samples. Four EC concentrations ranging from 23 to 240 µg/m^3 (EC loadings from 2.7 µg/cm^2 to 27 µg/cm^2) were generated. Again, analytical results indicate that the method meets the NIOSH accuracy criterion. The variance was roughly proportional to mean concentration; therefore, the S_r decreased with increasing concentration. The accuracy was calculated accordingly. The pointwise accuracy was ± 16.7% at the lowest loading (2.7 µg/cm^2) and the overall precision ($\ddot{O}_{rT}$) was 0.085.

When the thermal-optical method was evaluated [1] only one instrument existed. More recently, a private laboratory [6] built additional instruments (14 total:10 in the U.S., 1 in Canada, 1 in Australia, 1 in Hong Kong, 1 in Belgium). An interlaboratory comparison [7] was undertaken. Nine laboratories participated in the study, including four in Europe that employ an alternative thermal technique based on coulometric detection of CO_2. For the comparison, carbonaceous aerosols were collected on quartz-fiber filters (8" x 10") and portions of the filters were distributed to the participating laboratories for analysis in triplicate. Prior to distribution of the filter portions, multiple analyses were performed across all filters to ensure matched sample sets. Two aqueous solutions containing OC standards also were included in the sample sets. These standards provided a check on the accuracy of the TC data as well as a check on the pyrolysis correction feature of the thermal-optical method (both standards char during analysis).

As seen in a previous study [4], good agreement (within 15%) between TC values reported by all laboratories was obtained. In the analysis of samples containing diesel particulate, reasonable agreement was seen between the EC results obtained by each method (variability of the thermal-optical method was about 8% and variability for the coulometric method ranged from 9 to 23%). However, the EC content found by the two methods differed significantly. Given the operational nature of such methods, significant between-method variability was expected. Significant differences in the OC-EC results obtained by different methods also were reported previously [4].

With all filter samples, coulometric results were positively biased *relative* to thermal-optical results. In addition, the coulometric method gave a true positive bias in the analysis of the OC standard solutions. About 52% and 70% of the carbon found in two aqueous solutions (sucrose and EDTA, respectively) were quantified as elemental, while EC contents of about 1% and 0.1% (respectively) were found by the thermal-optical method. The positive bias in the results for OC standards is attributed largely to inadequate removal of all OC during the first part of the analysis (maximum temperature ~ 550 EC); lack of correction for pyrolysis (char) also is a factor. Because no increase in transmittance was seen during the first stage (helium only) of thermal-optical analysis, use of a higher maximum temperature during this stage did not appear to cause loss of light-absorbing carbon. This implies that the EC results (filter samples) obtained with the coulometric method are positively biased. Elevating the maximum temperature of the thermal program

gave better agreement with the thermal-optical method.

When a diesel particulate sample contains no other type of carbonaceous particulate and the OC fraction is essentially removed below about 500 EC, better agreement between methods is expected. Good correlation [8] was seen between results of thermal-optical and coulometric methods in the analysis of 22 samples collected in a simulated mining environment. The two methods gave essentially equivalent results for TC, with the coulometric method finding about 6% less than the thermal-optical. The small differences between TC results obtained by the two methods, even after shipping and handling by three laboratories, indicates TC measurement is accurate. Based on a previous comparison [7], this result was expected. Differences in the EC and OC results were again seen, but were much smaller than those obtained previously [7]. Mean EC fractions (i.e., EC/TC) of 0.53 and 0.46 were obtained by the coulometric and thermal-optical methods, respectively. The relatively minor difference is attributed to the different thermal programs used. Neither charring nor loss of a significant amount of carbon above 500 EC (and up to 850 EC in helium) were noted in the thermograms (i.e., output signal of thermal-optical instrument), which was not the case in the previous comparison [7].

The thermal-optical method is applicable to nonvolatile, carbon-containing species only. The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection. A complete discussion on the evaluation of this method for monitoring occupational exposures to particulate diesel exhaust in general industry can be found in the literature [1]. Different sampling requirements usually are required in the mining industry (see APPENDIX B).

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APPENDIX A. GENERAL

Diesel exhaust has been classified by IARC as a probable human carcinogen [9]. NIOSH has recommended "...that whole diesel exhaust be regarded as a potential occupational carcinogen..." and that workers' exposures be reduced [10,11].   Because diesel exhaust is a chemically complex mixture containing thousands of compounds, some measure of exposure must be selected. Rationale for selection of EC has been provided elsewhere [1].

The American Conference of Governmental Industrial Hygienists (ACGIH) has proposed a TWA of 0.15 mg/m^3 for diesel particulate [12]. The TLV is expressed in terms of submicrometer particulate matter, which includes the solid carbon core of diesel particulate and particle-adsorbed components. Other submicrometer aerosols will be collected as well (see APPENDIX B).

In general, three methods have been used for monitoring exposures to DPM: submicrometer particulate mass (gravimetric), respirable combustible dust (RCD; also gravimetric), and EC. These methods are mentioned in the draft TLV documentation, but the latter two (RCD and EC) do not give a direct measure of the stated analyte (submicrometer particulate). The RCD method targets the *respirable* fraction, not just submicrometer, and it is not a specific measure of DPM. The EC method is highly selective for diesel particulate, but the EC fraction of diesel particulate is variable, so a single constant cannot be used for extrapolation to submicrometer mass. Use of TC as a measure of diesel particulate has been considered because there is less variability in the carbon content of DPM. Although the TC fraction of DPM is relatively constant (typically 85% or more), other OC sources can interfere with the determination of the diesel-source carbon. A discussion of analytical methods is provided in the next appendix (APPENDIX B).

APPENDIX B. GUIDELINES ON METHODS

Gravimetric methods for DPM target submicrometer aerosol because diesel particulate is largely submicrometer and interference of larger dusts is minimized; however, if other submicrometer aerosols are present (e.g., cigarette smoke or other combustion aerosols, condensation aerosols) they will interfere in the gravimetric determination of diesel particulate. With personal monitoring, this approach is limited to relatively high concentrations because of poor sensitivity. This applies to the traditional gravimetric approach, as well as a "respirable combustible dust" (RCD) method used in the Canadian mining industry. RCD involves gravimetric determination of the combustible material on a silver membrane (or quartz-fiber) filter. The filter is weighed pre- and post-combustion, and the difference is considered RCD. This method is subject to interferences from non-diesel, respirable combustible matter and other potential problems (e.g., hygroscopic materials, negative bias with metal oxide formation).

A suitable impactor for personal monitoring of submicrometer particulate mass concentrations is not commercially available. A specialized impactor with a 0.8-µm cutpoint has been applied for the gravimetric determination of diesel particulate in underground coal mines. The cutpoint was based on bimodal particle size distributions found in dieselized underground coal mines, which is the only environment where the impactor must be used. Although it excludes most of the coal dust while collecting most of the diesel particulate, some sub-0.8-µm coal dust is collected. To determine the potential contribution of sub-0.8-µm, coal-source EC, laboratory studies and surveys of underground coal mines were conducted. When sampling a laboratory-generated, respirable coal dust concentration of 1.5 mg/m^3, a submicrometer TC concentration of about 54 µg/m^3 was found, but the corresponding EC concentration was only about 8 µg/m^3. Even when

the concentration of respirable coal dust was as high as 5 mg/m^3, which is more than 2.5 times the US compliance level, only a relatively low EC concentration was seen (EC = 30 µg/m^3; TC concentration = 156 µg/m^3). These results are in good agreement with those found in preliminary field studies. Only low levels (#15 µg/m^3) of EC were found in non-dieselized underground coal mines when a submicrometer cutpoint was used [13], indicating that the thermal-optical method could be applied in coal mines with only a minor contribution of coal-source EC if an impactor with appropriate design specifications is used. It is important to emphasize that the cutpoint of the prototype impactor was based on particle size distributions found in *coal mines*. Size distributions (of both diesel and non-diesel particles) found in coal mines may differ from those found in metal/nonmetal mines. With respect to diesel particles in particular, distributions might differ because water scrubbers are used in coal mines and these may affect particle size (e.g., by trapping larger respirable particles). If larger (e.g., 1 to 2 µm) diameter particles are present, these will be excluded if an impactor with a submicrometer cutpoint is used.

Unlike submicrometer particulate, RCD and TC, EC is a specific marker of occupational exposure to diesel particulate, so use of an impactor is unnecessary (except in coal mines). In some workplaces, a preclassifier (e.g., cyclone) should be used with a 37-mm cassette (or alternative cassette giving an even deposit) as a "sample cleanup" step (e.g., to reduce loadings of inorganic dusts), but a submicrometer cut is not necessary. Although uneven deposition of larger particles (i.e., non-diesel) can occur, an even deposit of DPM is ordinarily found. If an uneven deposit should form, the entire filter must be analyzed (in portions) to quantify the total OC and EC.

Different samplers can be expected to give equivalent results for EC because diesel exhaust is a combustion aerosol (particle diameters generally # 1 µm). As such, particles will be evenly deposited on the filter and collected with the same efficiency (near 100%). To confirm this assumption, seven different sampler types (open-faced, 25-mm and 37-mm cassettes; 298 personal cascade impactor (7 stages, 0.9 µm cutpoint); 4 prototype impactors) were used to collect diesel aerosol at the loading dock of an express mail facility. The S$_r$ of the mean EC concentration found was only 5.6% [1]. Higher variability (about 12%) was seen in the OC result, which is expected when using filters to collect aerosol containing volatile and semivolatile components. Similar results were obtained when collecting samples in an underground molybdenum mine, where non-diesel particulate also was present. Five different sampler types were used (closed-face, 25-mm and 37-mm cassettes; 298 (7 stages, 0.9 µm cutpoint); cyclone with filter; in-house impactor). The S$_r$ of the mean EC concentration found (297 µg/m^3) was only 7%. An even deposition of EC was obtained with all five sampler types, even when the deposit of other mine particulate was visually heavier in the center of the filter (e.g., with the closed-face 37-mm cassette). These results indicate that any of a variety of samplers can be used in some environments. In trona and limestone mines, a cyclone should be used to reduce the amount of carbonate collected (non-respirable-sized particles in particular). Specificity of the OC (and TC) determination can be further improved by removal of carbonate through acidification of the sample portion (see APPENDIX C). In the case of carbonates and other types of carbonaceous dusts, an impactor can improve the selectivity of the OC (and TC) measurement, but it could exclude a portion of the diesel particles. Some OC interferences cannot be excluded on the basis of size (e.g., condensation aerosols, fumes, wood and cigarette smokes).

APPENDIX C. THERMAL-OPTICAL ANALYZER DESIGN AND OPERATION

In the thermal-optical analysis of carbonaceous aerosols, speciation of organic and elemental carbon is accomplished through temperature and atmosphere control, and by continuous monitoring of filter transmittance. A schematic of the instrument is given below (Figure 1). The instrument is a modified version of a design previously described in the literature [14]. An optical feature corrects for pyrolytically generated elemental carbon (EC), or "char," which is formed during the analysis of some materials (e.g., cigarette and wood smokes, pollen). Laser light passed through the filter allows continuous monitoring of filter transmittance. Because temperatures in excess of 850 ᵉC are employed during the analysis, quartz-fiber filters are required. A punch from the sample filter is taken for analysis, and organic and elemental carbon are reported in terms of µg per cm^2 of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous sample deposit is assumed. Just prior to the end of the analysis (i.e., after EC is evolved), calibration is achieved through injection of a known volume of methane into the sample oven.

Thermal-optical analysis proceeds essentially in two stages. In the first, organic and carbonate (if present) carbon are evolved in a helium atmosphere as the temperature is stepped to about 850 EC (750 EC if EC loss is evident). The evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2, then reduced to CH_4 in a Ni/firebrick methanator. CH_4 is quantified by an FID. In the second stage, the sample oven temperature is reduced, an oxygen-helium mix is introduced, and the temperature is stepped (to about 940 EC). As oxygen enters the oven, pyrolytically generated carbon (PC) is oxidized and a concurrent increase in filter transmittance occurs (see Figure 2). The point at which the filter transmittance reaches its initial value is defined as the "split" between OC and EC. Carbon evolved prior to the split is considered OC (including carbonate), and carbon volatilized after the split is considered elemental (EC).

The presence of carbonate is verified by exposing a second punch from the filter to HCl vapor prior to analysis. A dessicator containing concentrated HCl (added to dessicator or a petri dish placed at the bottom of it) can be used to acidify the punches. The dessicator, or alternative vessel, should be used in a well-ventilated hood. Place punches on the dessicator tray, put tray in dessicator and cover with lid. A wetted pH indicator stick can be used to check acidity. A wetted indicator stick inserted between the dessicator lid and base should give a pH near 2. Expose punches to vapor for about 1 h (large particles can require more time). After acidification, remove the tray and place it on a clean surface inside a hood. Allow the residual acid on the punches to volatilize in hood for at least one hour before analyzing. When the acidified sample is analyzed, a much-reduced (or absent) peak is indicative of carbonate in the original sample. The difference between the TC results obtained for the two punches (i.e., before and after acidification) gives an estimate of carbonate-source carbon (presuming it is evenly deposited on the filter). The acidified sample results provide a better measure of the diesel-source OC (and TC) if the sample contains carbonates. Acid treatment may change the appearance of the carbon profile, but the EC result itself should not be affected significantly. More recent versions of the calculation software allow estimation of carbonate carbon through integration, but this applies only in cases where the carbonate can be removed as a single peak during the fourth temperature step (e.g., calcium carbonate). If the integration feature is used, always verify that the carbonate of interest is removed as a single, unique peak.

Currently, three laboratories [6,15,16] perform thermal-optical analysis on a commercial basis. The commercial availability of the instrument is limited to a single supplier [6] and its design continues to be improved. An evaluation of a newer design is planned.
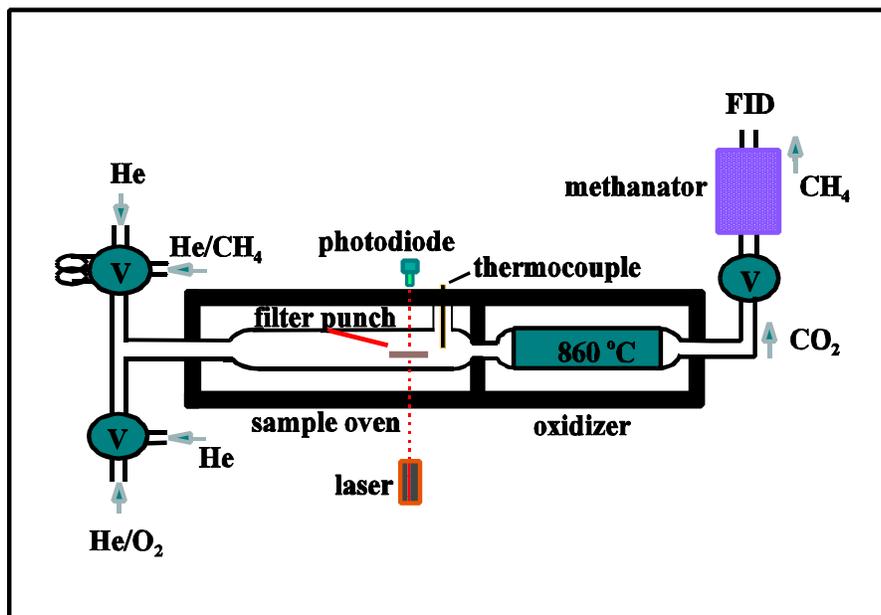
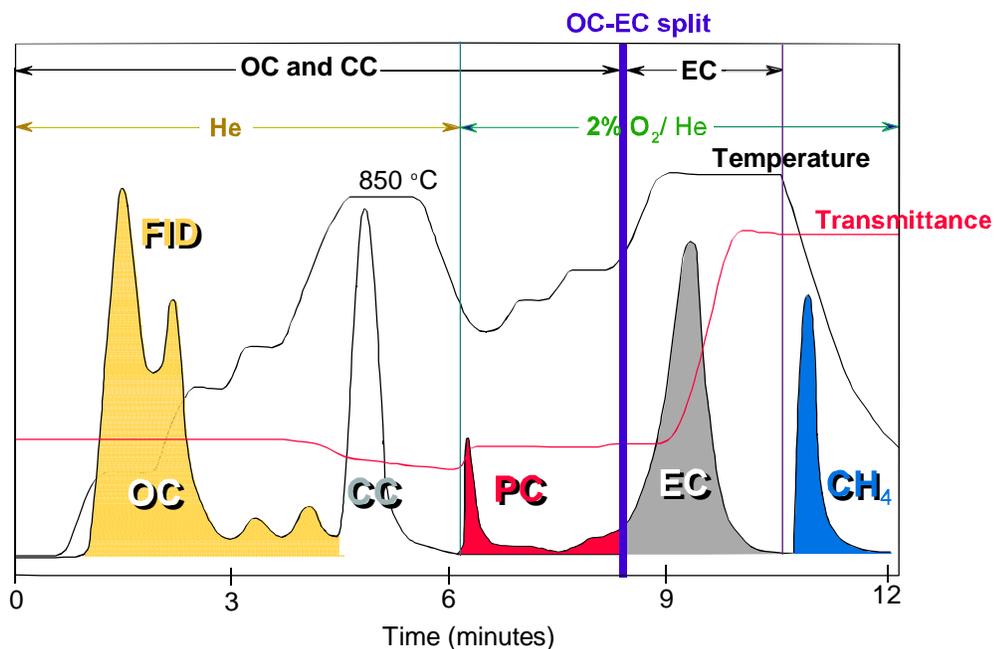**Figure 1.** Schematic of Thermal-Optical Instrument (V=valve)

Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate.