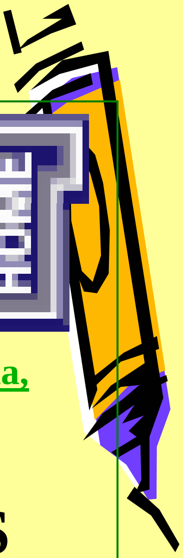
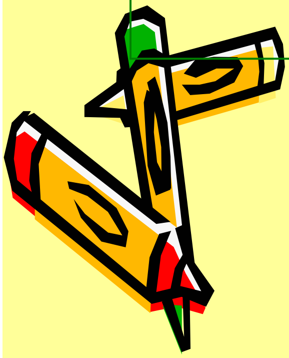


University of Nevada, Reno

MELTING POINT INDICATORS FOR CALIBRATING THERMAL/OPTICAL CARBON ANALYZERS.

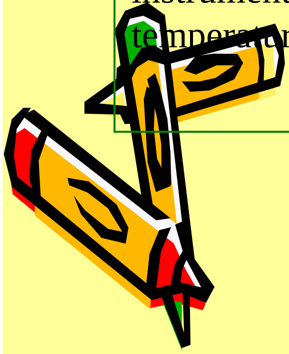
Guadalupe Paredes-Miranda, Lung-Wen Antony Chen, Oliver Chang, Judith C. Chow, and John G. Watson*.

Desert Research Institute (DRI/UNR), 2215 Raggio Parkway, Reno, NV 89512, USA

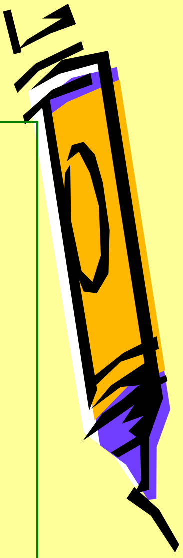


ABSTRACT

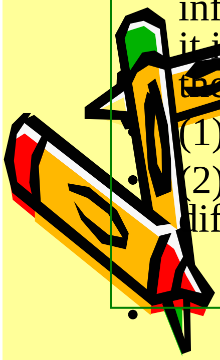
Thermal/optical methods have been widely used for analyzing the carbon content in ambient and source particulate samples. Particles deposited onto filter substrates (e.g., quartz, glass, or aluminum) are heated to designated temperatures in either inert or oxidizing atmosphere, and carbon evolved is converted to CO2 or CH4 and quantified. The more volatile carbon fraction that evolves at a lower temperature is referred to as organic carbon (OC), in contrast to elemental carbon (EC) that is oxidized at a higher temperature. Optical properties of filter samples (e.g. reflectance or transmittance) are monitored to correct for charring of OC during heating. The choice of combustion temperatures is important to the thermal/optical analysis since 1) the partition of OC and EC depends on the temperature protocols and 2) carbonaceous materials from various sources evolve or chare at different temperatures due to different molecular structures. The appropriate selection of temperature maximizes information about the origin of the carbon. In most cases the temperature is determined by a thermocouple placed near the sample. However, due to the inhomogeneities of temperature in the furnace, different thermal properties of the sample and the sensor, and response delays of the thermocouple, the thermocouple reading may not represent the actual sample temperature nor the heating rate. Sample temperatures are related to thermocouple temperatures using a melting point standard, that changes its appearance when a certain Tempilaq (Tempilaq°G Indicating Liquid, Unit E Agoura Hills, CA 91301) coating is spread on a blank filter, and the change in appearance is detected by filter reflectance and transmittance. The thermocouple readings are registered, under both heating and cooling, and compared with the known Tempilaq melting point temperature. Differences between thermocouple reading and melting point standard, when applied to DRI Model 2001 Thermal/optical Carbon Analyzers vary from –8.0°C to +2.6°C. The thermocouples are re-calibrated so the temperature relations for all instruments are the same with a statistical uncertainty of about ±1.6°C. The technique can be applied to any thermal/optical instrument to evaluate deviations from assured temperatures or to calibrate the temperature sensors to better represent sample temperatures.

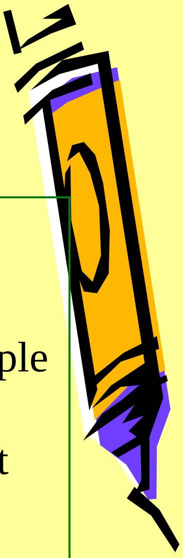


Introduction



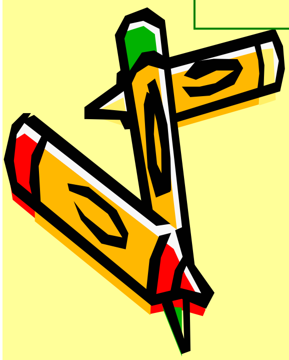
- Carbonaceous material has been identified as a major component of ambient fine aerosol from remote to urban environment and is involved in various aerosol health, visibility, and climate impacts (Vedal, 1997; Watson, 2002; Jacobson, 2001). It consists mostly of elemental carbon (EC), which is emitted directly into the atmosphere during incomplete combustion, and organic matter. EC has a chemical structure loosely related to graphite, is non-volatile at ambient conditions, and absorbs strongly at visible, near-infrared (IR), and near-ultraviolet (UV) wavelengths. On the other hand, organic matter can be emitted directly by sources or can be formed in the atmosphere through condensation of low-volatility oxidation products of hydrocarbons. Organic carbon (OC) is the carbon fraction of organic matter, and is, by itself, weakly light-absorbing in the visible region.
- Aerosol total carbon (TC), EC, and OC are often quantified by thermal/optical methods (Huntzicker et al, 1982; Chow et al, 1993; Peterson & Richards), which release carbon collected on a filter (e.g., quartz-fiber) through heating/oxidation and convert it to carbon dioxide (CO2) or methane (CH4) for detection. Since EC has low volatility, it is not released without oxygen (O2) at a temperature below ~700 0C and thereby can be separated from OC. However, heating in a oxygen-free environment causes certain OC components to pyrolyze and form non-volatile, light-absorbing char that could be mistaken for EC. This bias is corrected by monitoring the reflectance or transmittance of a filter matrix during thermal analyses.
- The appropriate selection of combustion temperature maximizes information about the origin of the carbon. Among other reasons, it is important to choose correctly the temperature in the thermal/optical analysis because:
- The appropriate selection of combustion temperature maximizes information about the origin of the carbon. Among other reasons, it is important to choose correctly the temperature in the thermal/optical analysis because:
- (1) The OC/EC split depends on the temperature protocols, and
- (2) Organic material from various sources evolve or chare at different temperatures due to different molecular structures.





Typically the temperature is determined by a thermocouple placed near the sample. However, the thermocouple reading may not represent the actual sample temperature. Several inaccuracies arise due to the inhomogeneities of temperature in the furnace, different thermal properties of the sample and the sensor, and response delays of the thermocouple.

- **<u>Objective.</u>**
- The main objective of the present work is to estimate the systematic and statistical errors associated to the thermocouple reading, for three different versions of the DRI Model 2001 thermal/optical carbon analyzer. Sample temperatures are related to thermocouple temperatures using a melting point standard, the non-flammable quick-drying liquid Tempilaq (Tempilaq0 G Indicating Liquid, Unit E Agoura Hills, CA 91301), as will be described in the experimental section.



Brief description of the DRI Model 2001 thermal/optical carbon analyzer.

- **Figures 1 and 2** show respectively a photo and an scheme of the thermal/optical carbon analyzer. As illustrated in figure 2, the usual thermal/optical carbon analysis is carried out by: (1) liberating carbon compounds at different temperature and oxidation environments from a small sample punch taken from a quartz-fiber filter, (2) converting these compounds to CO_2 by passing the evolved carbon through a manganese dioxide (MnO_2) oxidizer at 912^{0}C, (3) reducing the CO_2 to CH_4 by passing the flow through a nickel catalyst methanator at ~440^{0}C, and (4) quantifying the CH_4 by flame ionization detector (FID).

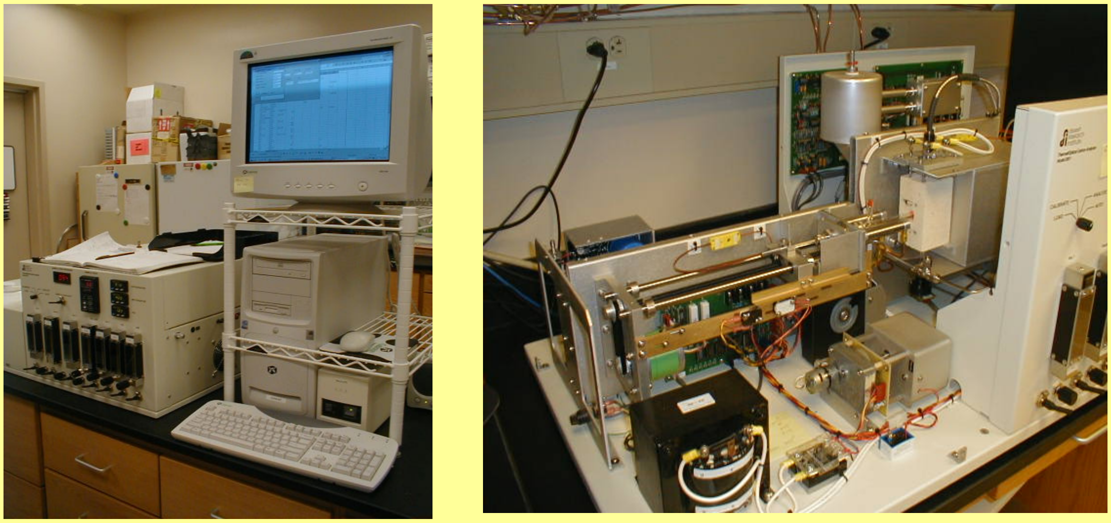


Figure 1. Shows one DRI Model 2001 #6 Thermal/Optical Carbon Analyzer and what is inside of each instrument.

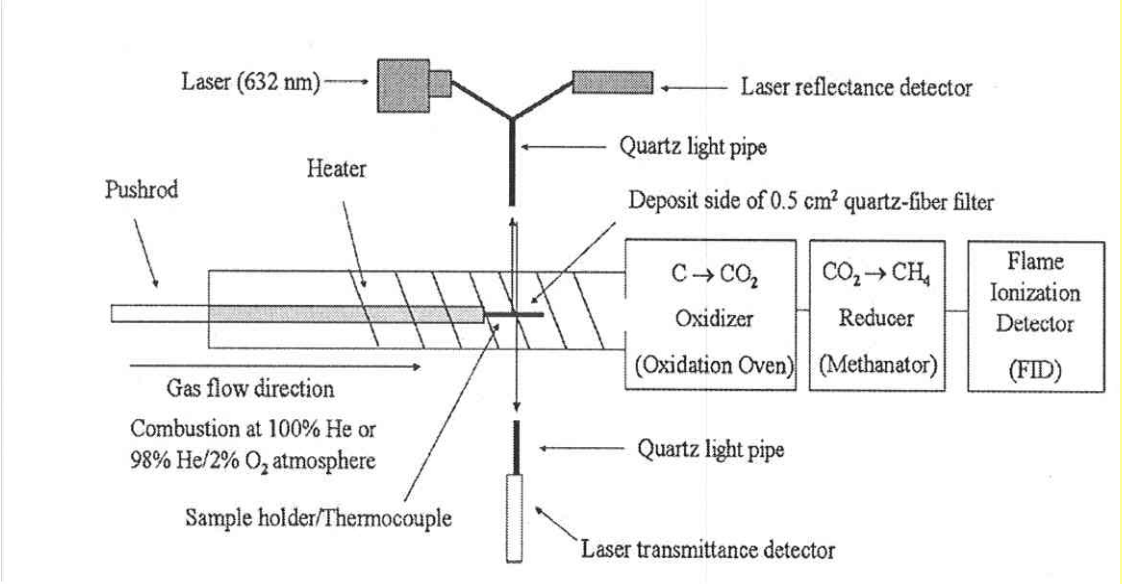
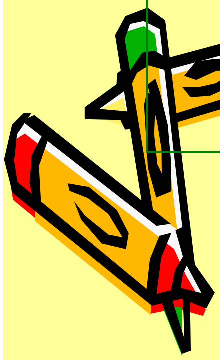


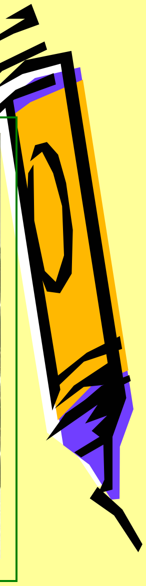
Figure2. Schematic diagram of a DRI Model 2001 Thermal/Optical Carbon Analyzer

- A He/Ne laser beam (623 nm wavelength) is directed toward the exposed side of the filter via a quartz light pipe. Direct forward and backward scattering of the radiation is detected by identical photodetectors on both sides of the filter to measure reflectance and transmittance throughout the analysis. Reflectance (R) and transmittance (T) are defined as the ratios of reflected and transmitted laser signals from a sample relative to the corresponding detector output with no sample present. For blank quartz-fiber filters (Pallflex 7202, Pall Laboratory, Ann Arbor, MI), the average R and T are found to be ~ 1.9 x 10-2 and ~ 4.5 x 10-3 respectively, and vary by <5% from filter to filter.
- Further details of the DRI Model 2001 thermal/optical carbon analyzer can be found elsewhere (Chen et al, 2003).
-

Experimental Section.

- For the purpose of estimating the systematic error, ΔT, in the thermocouple reading (i.e., ΔT is the difference between the actual sample temperature and the value measured by the thermocouple) we work with the thermal/optical part of the analyzer, without making use of the carbon detector part (oxidizer, reducer, FID). As explained in the objective, a quick-drying temperature-sensitive indicating liquid Tempilaq was used as a melting point standard. Figure 3 is a photo of some of the Tempilaq liquids as received. Table 1 lists the details and the melting temperatures of several varieties of Tempilaq used in our experiments. In the following we describe the experimental procedure of the temperature calibration.
- A previously baked membrane filter is cut in a small square, approximately 1.3 x 1.3 inches using a razor blade. The squared filter is deposited in a Petri dish, and split in two parts using two pairs of forceps. Both parts of the filter are put on a weighing paper (4 x 4 inches) on the Petri dish to reduce spillage when applying the Tempilaq. The liquid is spread over each surface with the provided brush, forming a thin coating which completely covers the surface and which very quickly dries (this operation should be carried out inside of a fume-hood). Depending on the Tempilaq liquid density and viscosity, we need to apply more or less coatings, according to Table 1. After covering both filter surfaces with Tempilaq, the two filter parts are joined, with the Tempilaq on the inside like a sandwich, and with a clean weighing paper covering the sandwich. Samples of known area (0.506 cm^2) are punched and weighted. Finally the sample is put on the boat of the carbon analyzer, holding always the sample with tweezers.





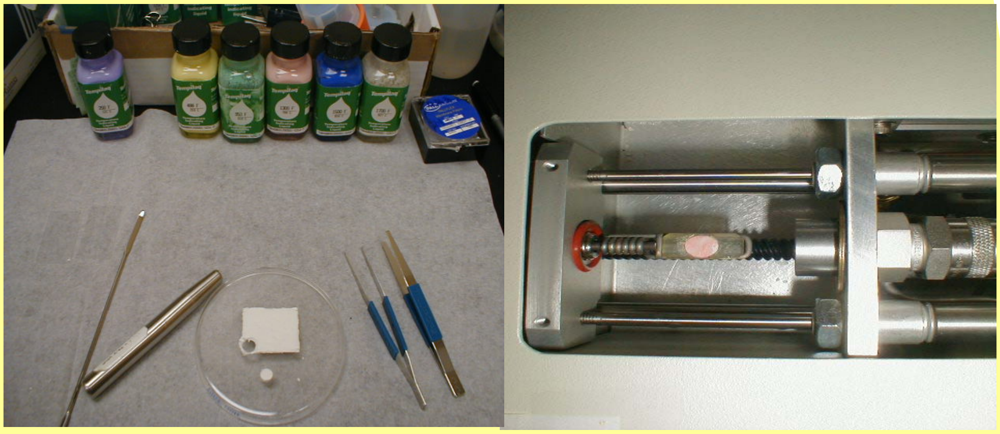


Figure 3. Shows temperature indicating products (TEMPILAQ) plus quartz filter punch plus a Tempilaq sample loaded in the carbon analyzer instrument.

Inside the instrument the sample and thermocouple are subjected to a temperature protocol trough the heater. Different temperature protocols were designed for different Tempilaq melting point. As an example we describe the protocol in the case where the Tempilaq melting point is 253 ^{0}C. In that case, the temperature is increased drastically until reaching 215 ^{0}C, and is further increased very slowly approximately linearly with time until, after about 1500 seconds, the temperature becomes 264 ^{0}C. Finally the sample is cooled very quickly.

During both heating and cooling the He/Ne laser beam is directed toward the sample, and both reflectance (R) and transmittance (T) are measured. A Microsoft Access computer program, connected to the photodetectors, registers the behavior of R and T as a function of time. Since temperature and time are directly related trough the corresponding temperature protocol, the resulting graphs can be interpreted as giving R and T as functions of temperature.

For every instrument and Tempilaq melting point temperature, the experiment is run four or five times so that an average and standard deviation can be obtained.

CHEMICAL NAME, CLASS:	**Temperature °C**	**Active Ingredients (%)**	**Approx. # of strokes on the first membrane's slide**	**Approx. # of strokes on the second membrane's slide**	**Comment**
TEMPILAQ-0250F	121	Hydrocarbon, c8-c11 (10-15) Toluene (15-20) 1,2 Butylene oxide (<0.6) Dimethoxymethane (1-5) n-Propyl bromide (50-60) t-Butanol (1-5)	11	10	Dries very fast, difficult to spread homogeneously
TEMPILAQ-0363F	184	Hydrocarbon, c8-c11 (10-15) Toluene (15-20) 1,2 Butylene oxide (<0.6) Dimethoxymethane (1-5) n-Propyl bromide (50-60) t-Butanol (1-5)	10	8	Similar to 121
TEMPILAQ-0488F	253	Hydrocarbon, c8-c11 (10-15) Toluene (15-20) 1,2 Butylene oxide (<0.6) Dimethoxymethane (1-5) n-Propyl bromide (50-60) t-Butanol (1-5)	12	10	Homogenous deposit possible is loaded.
TEMPILAQ-0950F	510	Hydrocarbon, c8-c11 (10-15) Toluene (15-20) 1,2 Butylene oxide (<0.6) Dimethoxymethane (1-5) n-Propyl bromide (50-60) t-Butanol (1-5)	25	20	Easy to apply but a double layer is loaded.
TEMPILAQ-1300F	704	Hydrocarbon, c8-c11 (10-15) Toluene (15-20) 1,2 Butylene oxide (<0.6) Dimethoxymethane (1-5) n-Propyl bromide (50-60) t-Butanol (1-5)	25	26	Less viscousity
TEMPILAQ-1500F	816	Hydrocarbon, c8-c11 (10-15) Toluene (15-20) 1,2 Butylene oxide (<0.6) Dimethoxymethane (1-5) n-Propyl bromide (50-60) t-Butanol (1-5)	32	20	Same as 704
TEMPILAQ-1700F	927	Hydrocarbon, c8-c11 (10-15) Calcium Sulfate (15-20) Sodium Sulfate (10-15) 1,2 Butylene oxide (<0.6) Dimethoxymethane (1-5) n-Propyl bromide t-Butanol	30	20	High temperatures Liquid not good for the quartz Boat.

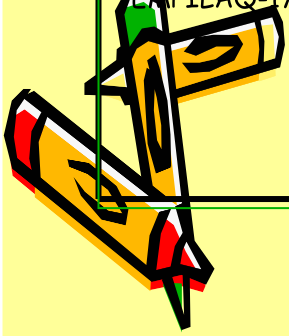


Table 1. Temperature indicating product information.

Results and Analysis.

Figures 4 and 5 are examples of our final experimental results, i.e., the reflectance R as a function of time for a run of the experiment. The reflectance time derivative is obtained in the following way: for any given time, the slope of the reflectance in an interval of about 200 sec., centered in that time, is calculated by linear regression. The reflectance time derivative curve is also shown in Figures 4 and 5.

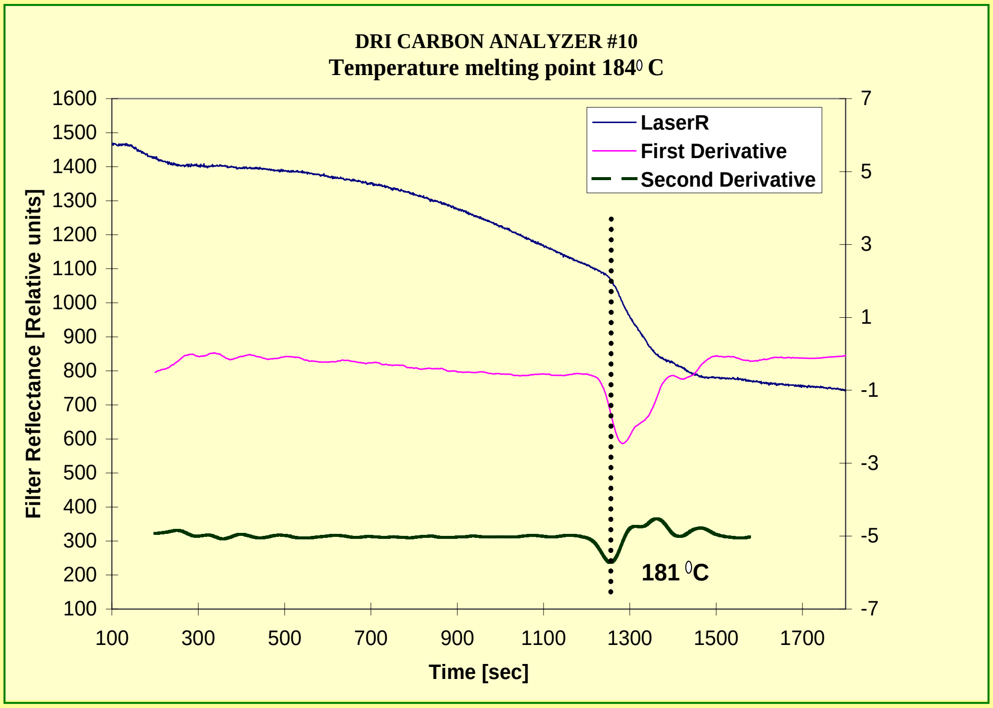
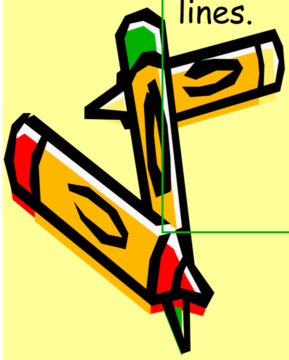
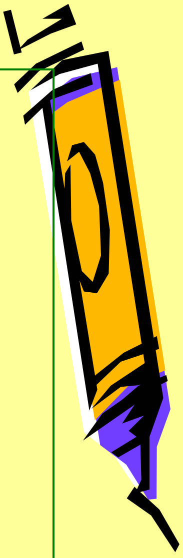


Figure 4. Shows reflectance as a function of time for a run (184 °C) of the experiment.

When the increasing temperature of the heater reaches the Tempilaq melting point temperature, the solidified Tempilaq coating is expected to fuse again, suffering a change in appearance that should be detected by filter reflectance and transmittance. In Figures 4 and 5 the period of time in which both reflectance and reflectance time derivative suffer a sudden change in behavior is enclosed between vertical straight lines.





This period of time should correspond to the moment in which the heater temperature equals the Tempilaq melting point, so the thermocouple reading corresponding to this time is the experimental estimation of the melting point temperature.

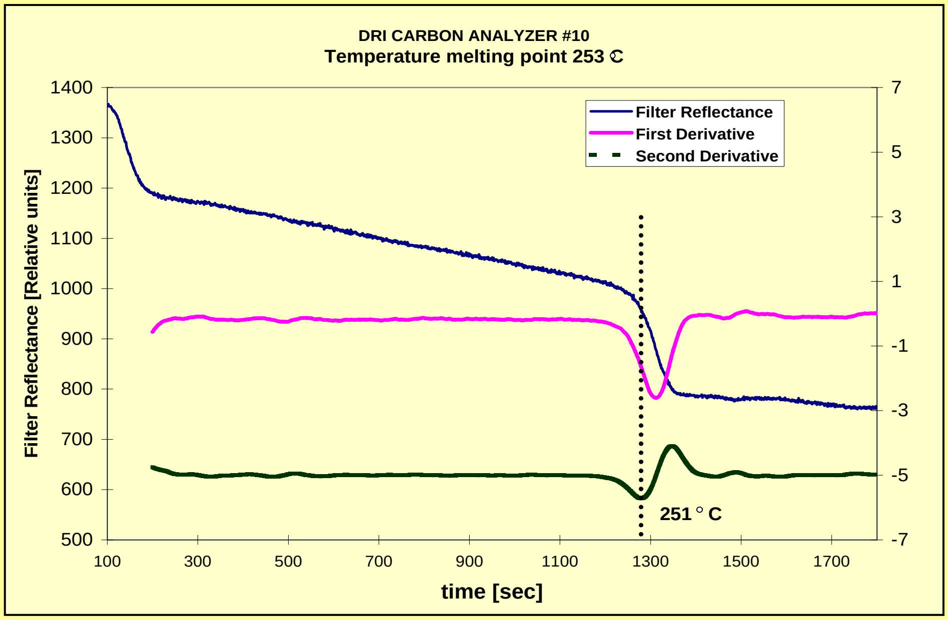
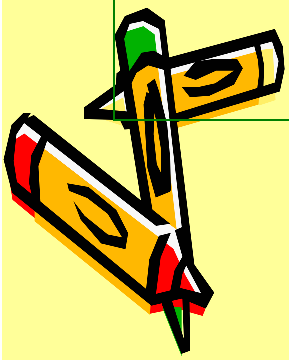


Figure 5. Shows reflectance as a function of time for a run (253 °C)

It should be noted that (1) the data points are close to the fitted straight line, and (2) the slope of such a line is very nearly one. These two results permit us to conclude that the thermocouple reading follow very close the Tempilaq melting point temperature, but it has a systematic error very approximately equal to the ordinate to the origin in the linear fitting. This is therefore our estimation of ΔT, the difference between the actual sample temperature and the value measured by the thermocouple.

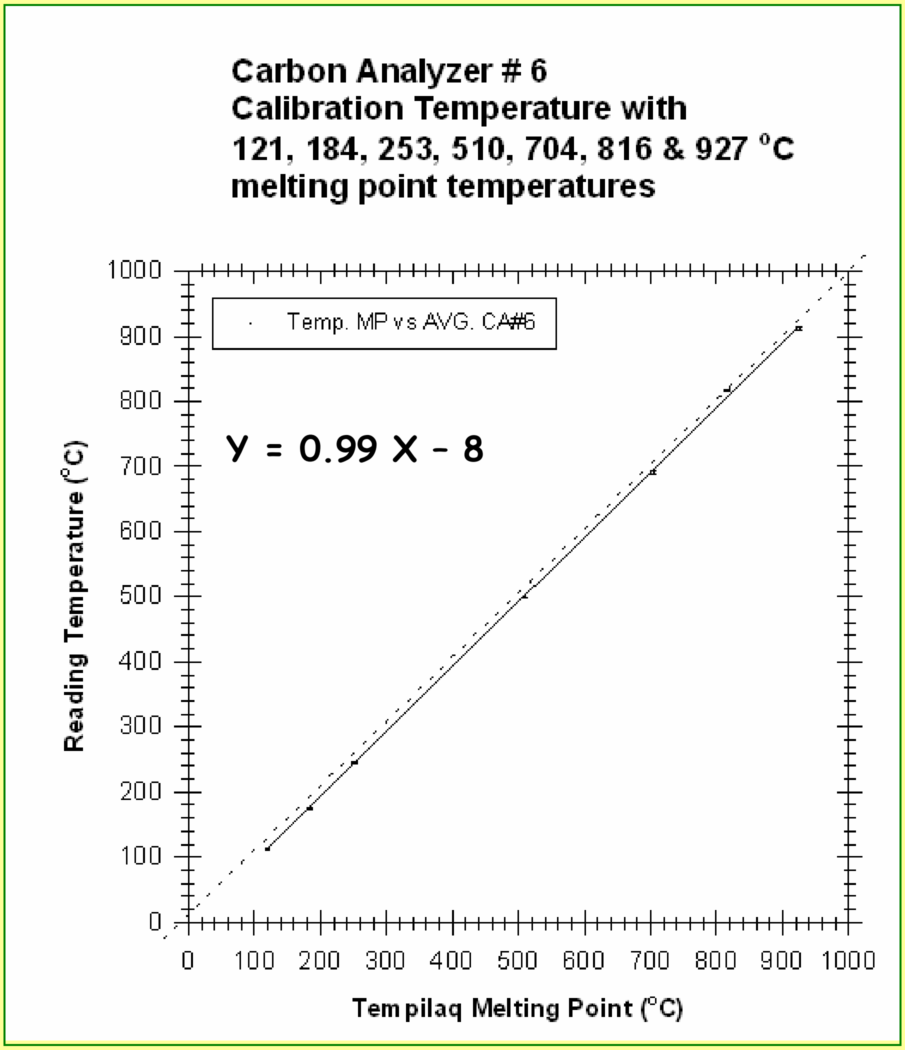


The uncertainties associated to every data point in Figure 6 were calculated as the statistical error (standard deviation) of the 4 or 5 measurements done for the same Tempilaq melting point temperature. The final reported uncertainty associated to ΔT is the average of the statistical errors of all data points for the same instrument.

For the instrument analyzed in **Figure 6**, the final estimation of the error in the temperature measurement is **ΔT = -7.9 ± 1.6.**

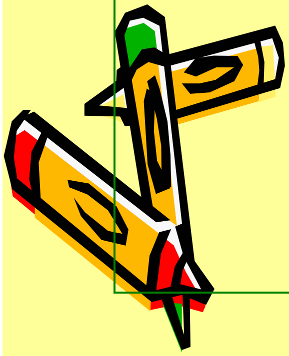
For the other two instruments the final results were

ΔT = 2.6 ± 1.1 (carbon analyzer #8) and **ΔT = -8.0 ± 1.9** (carbon analyzer #10) respectively.



Carbon Analyzer # 6
Calibration Temperature with
121, 184, 253, 510, 704, 816 & 927 °C
melting point temperatures

Figure 6. Final results for DRI carbon analyzer #6.



Conclusions.

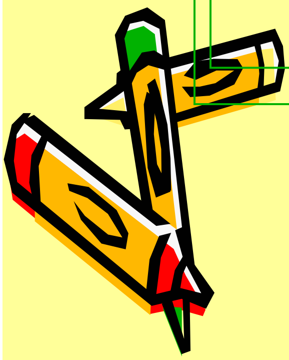
We are trying to estimate the difference ΔT between the actual sample temperature and the thermocouple readings for three different DRI 2001 Model Thermal/Optical Carbon Analyzers. In order to do this, we used a melting point standard, that changes its appearance when a certain Tempilaq coating is spread on a blank filter, and the change in appearance is detected by filter reflectance. Seven Tempilaq indicators with their corresponding melting point temperatures were used.

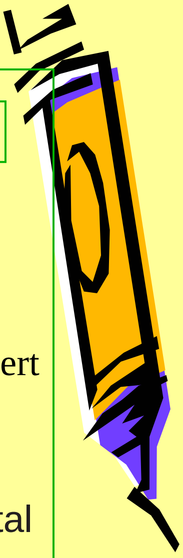
In every measurement a graph of reflectance against time is obtained. The reflectance time derivative is obtained in the following way: for any given time, the slope of the reflectance in an interval of about 200sec., centered in that time, is calculated by linear regression. The temperature is estimated by observing the time interval in which the reflectance derivative has a sudden change.

For every indicator, four or five measurements were carried out, and the statistical average and standard deviation were calculated.

The data of temperature readings so obtained are plotted against Tempilaq melting point (for every instrument). We made a linear regression of this data points, obtaining a straight line with a slope very close to 1. We conclude that the ordinate at the origin of this linear regression is a good estimation for ΔT. For the different instruments, we obtained a ΔT varying from –8.0°C to +2.6°C.

The associated uncertainty of ΔT was computed with the (averaged) statistical error (standard deviation) of the 4 or 5 measurements done for the same Tempilaq melting point temperature, obtaining an uncertainty which varies between 1.6 and 1.9, depending on the corresponding instrument.





References

(1) Supplier/ Manufacturer:Tempil Inc. 2901Hamilton Blvd. South Planfield, NJ 07080

(2) DRI Standard Operating Procedure, DRI SOP #2-204.6, Desert Research Institute.

(3) L.-W. Antony Chen; J.C. Chow; J.G. Watson; H. Moosmuller,;W. Patrick Arnott; Modeling reectance and transmittance of quartz-berlter samples containing elemental carbon particles:Implications for thermal/optical analysis; Eds.; J. Aerosol Sci. Technol (article in Press), 2003