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Author

Benner, W.H.

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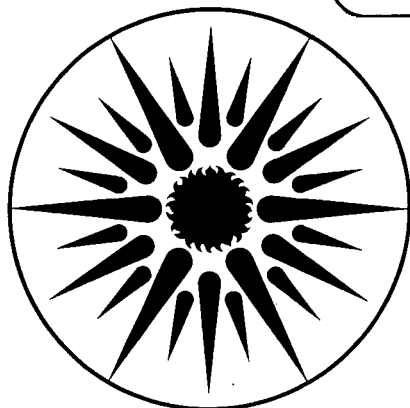
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DETERMINATION OF ORGANIC OXYGEN IN AMBIENT PARTICULATE MATTER*

W.H. Benner, A.D.A. Hansen, L.A. Gundel, and T. Novakov

Applied Science Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

ABSTRACT

A sample of ambient particulate matter is pyrolyzed in N_2 at $1135^\circ C$, and the evolved oxygen is detected by nondispersive infrared spectrometry after conversion to CO. Oxygen in organic compounds, carbonates, silicates, sulfates, nitrates, water, and adsorbed oxygen-containing gases is quantitated; but silica and alumina are not detected. Organic oxygen is determined by analyzing an evaporated extract of the sample. A procedure is also presented for determining oxygen thermograms. The organic fraction of ambient particulate matter is highly oxygenated ($C/O \approx 2$).

INTRODUCTION

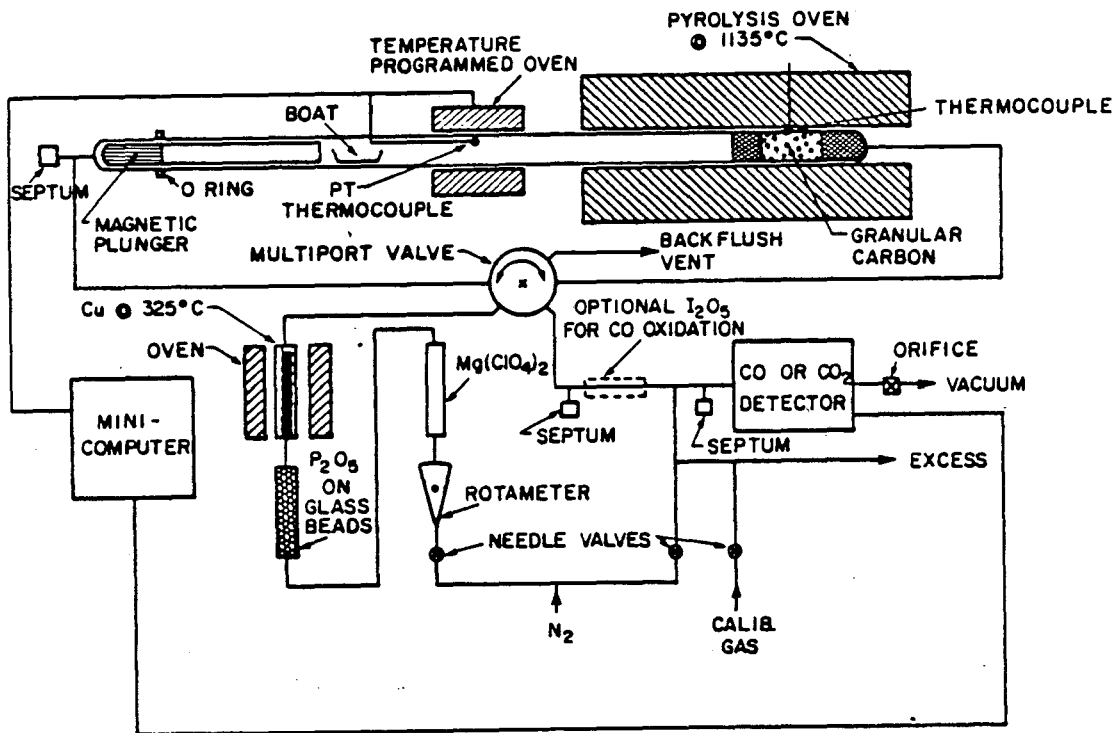
A technique has been developed to determine the concentration of pyrolyzable oxygen in filter samples of atmospheric particulate matter. Pyrolyzable oxygen is determined by quantitating the amount of oxygen that is evolved when a sample is thermally decomposed in N_2 after conversion to CO. It has been found that (pyrolyzable oxygen/total oxygen) ≤ 1 and that this ratio is dependent on the decomposition temperature and the substance of interest. This technique, when combined with solvent extraction of a sample, can be used to determine the organic oxygen in ambient particulate matter.

METHOD

We have modified a pyrolysis technique that was first described by Schutze (ref.1) and others (refs.2,3) so that microgram quantities of oxygen can be determined. The apparatus is shown in Fig. 1 and consists of three principal components: 1) a quartz pyrolysis tube in which a sample is thermally decomposed under N_2 and in which a bed of granular carbon is contained, 2) ovens that are used to heat the carbon and/or decompose the sample, and 3) a nondispersive infrared CO detector, coupled to a small computer, to quantitate oxygen in the decomposition products.

CO_2 samples are injected via a septum and are used to check the performance

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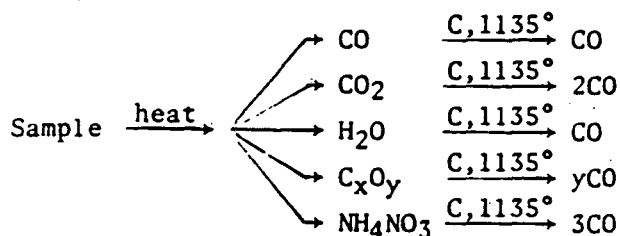


XBL 833-126

Fig. 1. Analytical apparatus for quantitating pyrolyzable oxygen and obtaining oxygen thermograms.

of the system. Filter samples are placed in a platinum boat and loaded into the cool zone of the pyrolysis tube during backflushing with N_2 . After entrained air is backflushed from the resealed system, a sample is slid into either of the ovens with a magnetically moved plunger. Oxygen analysis can be performed optionally in two modes, depending on which oven the sample is placed in. One oven is maintained at $1135^\circ C$ to heat the carbon. If the sample is placed in this oven, pyrolyzable oxygen (O_p) is quantitated. A separate oven is temperature programmable from room temperature to $1135^\circ C$ and is used to obtain an oxygen thermogram of the sample. This second mode of operation quantitates the oxygen released from a sample as a function of temperature.

Oxygen in the decomposition products is forced through the bed of hot carbon and is converted to CO in the reducing atmosphere. The evolved CO is then quantitated by drawing it through a nondispersive infrared CO detector. Examples of analytical reactions are:



1 atom O $\xrightarrow{\text{heat, C at } 1135^\circ C}$ 1 molecule CO

Oxygen in ambient particulate matter in general exists as organic oxygen, carbonates, silicates, sulfates, nitrates, metal oxides, water, and adsorbed gases like CO_2 and O_2 . This technique will detect oxygen in all species that decompose at $T < 1135^\circ\text{C}$. Refractory oxides like silica and alumina will not decompose at this temperature, but OH functional groups on the surface of many silicious materials will decompose.

EXPERIMENTAL

Analysis of O_p in a number of standard compounds, including NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, 2,4-dihydroxybenzaldehyde, p-diethoxybenzene, benzoic acid, m-hydroxybenzoic acid, CO_2 , glutaric acid, myristic acid, phthalic acid, and potassium phthalate (KHP), showed an overall recovery of $101.8 \pm 4.5\%$ ($\bar{x} \pm \text{s.d.}$) of the expected oxygen for 22 standards in the 7-46 $\mu\text{g O}$ sample size range. The limit of detection (blank + $3 \sigma_{\text{blank}}$) is 10.9 $\mu\text{g O}$. Analysis of microliter injections of CO_2 showed a $100.0 \pm 0.4\%$ recovery.

Filter samples of ambient particulate matter were collected in Berkeley, California, and Riverside, California, by hi-volume sampling onto pre-fired quartz fiber filters. The Berkeley samples were 24-hr samples collected between May and November 1978. The sampling dates of the Riverside samples are shown in Table 1. A portion of the filters had been sequentially extracted in benzene

TABLE 1

Analysis of solvent extracts of filter samples collected in Riverside, California.

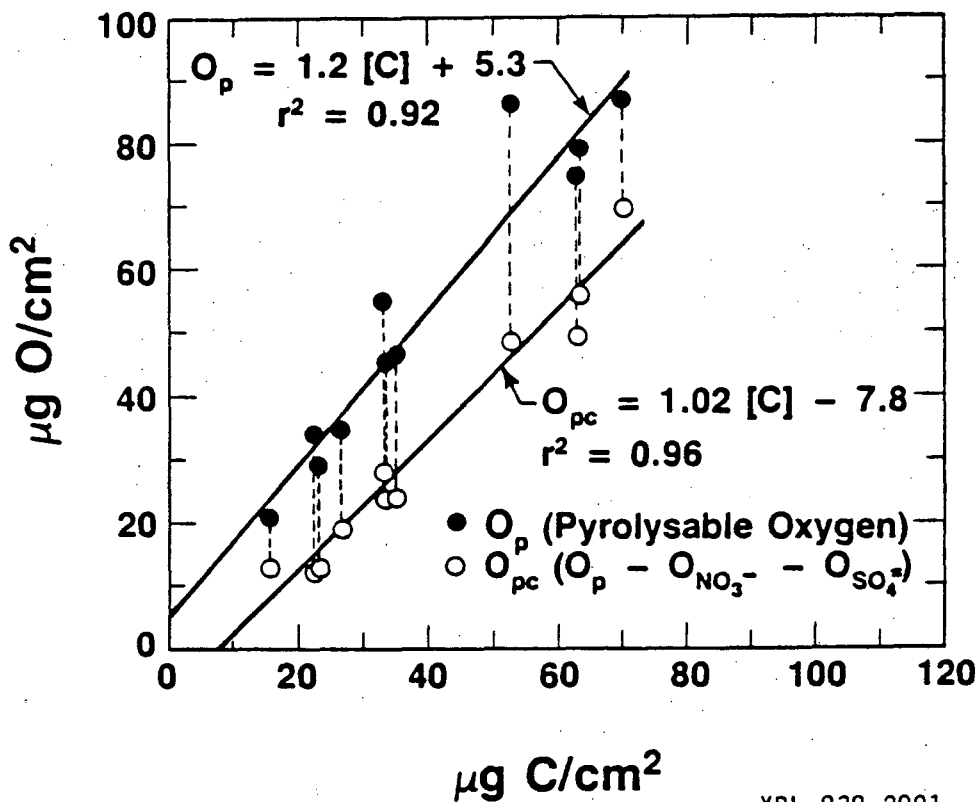
Sample	Time/date	Wt. basis		Atomic basis	
		C/ O_{PC}	C/ O_{PC}	$\mu\text{g C}/\text{m}^3$	$\mu\text{g O}_{\text{PC}}/\text{m}^3$
UCR-1	1830 16 Jun 81-	1.54	2.1	11.2	7.3
	0600 17 Jun 81				
UCR-2	0635 17 Jun 81-	1.76	2.3	29.9	17.0
	1632 17 Jun 81				
UCR-7*	1035 16 Jun 81-	1.17	1.6	7.7	6.6
	1830 16 Jun 81				
UCR-8*	1830 16 Jun 81-	1.28	1.7	8.2	6.4
	0600 17 Jun 81				

*Size-segregated inlet on sampler so that $D_p < 1.3 \mu\text{m}$ collected.

and then in methanol-chloroform (1:2) for a previous study (ref.4). Filters and available extracts were analyzed for O_p , C, NO_3^- , and $\text{SO}_4^{=}$. Carbon was determined by combustion, and NO_3^- and $\text{SO}_4^{=}$ were determined by ion chromatography. Corrected pyrolyzable oxygen ($\text{O}_{p,c}$) is the pyrolyzable oxygen concentration from which the concentrations of oxygen in NO_3^- and $\text{SO}_4^{=}$ are subtracted.

In Fig. 2, O_p and $\text{O}_{p,c}$ are plotted versus C for a set of filter samples collected in Berkeley, California. The slope of the linear regression line shows that $\text{O}_{p,c}/\text{C} = 1$. Since carbon is a major component of ambient particulate matter, composing 4-40% by weight of the total particulate matter (ref.5), this

Unextracted Berkeley Filter Samples



XBL 838-2991

Fig. 2. Analysis of filter samples collected in Berkeley, California. Each datum point was from 1 cm² of filter.

ratio indicates that oxygen is also a major component. In fact, oxygen composes an even larger fraction of the particulate matter because this analytical technique does not quantitate oxygen in silica and alumina. Figure 2 also indicates the relative amount of oxygen in the forms of NO₃⁻ and SO₄⁼ oxygen. The data in Fig. 2 are plotted as a quantity of O per cm² of filter and in actual analysis represent the quantity determined from the analysis of 1 cm² of filter. This points out the sensitivity of the technique.

$O_{p,c}$ and C were determined in the solvent extracts of several filter samples collected in Riverside, California (Los Angeles air basin). The data are represented in Table 1. The extracts analyzed in Table 1 were first filtered through a Teflon filter to remove insoluble particles and quartz filter fibers and then concentrated by evaporation under N₂. A 10-µl aliquot of the concentrated extract, corresponding to ~ 4 cm² of original filter, was evaporated onto a 1-cm² disc of prefired quartz fiber filter. On an atomic basis, C/ $O_{p,c}$ in the extracts has an average of 1.9 and indicates that the soluble organic material associated with ambient particulate matter is highly oxygenated. This ratio suggests that the average formula for soluble oxygenated-carbonaceous material is ~ (C_{1.9}O)_n. A number of oxygenated-hydrocarbons found in smog chamber

aerosols have C/O ratios within the range of those ratios in Table 1 in ref. 6. Comparison of UCR-1 and UCR-8 shows that the particles having $D_p < 1.3 \mu\text{m}$ are more oxygenated than the non-size-segregated sample. The C/O ratios in source particulate matter have not yet been determined. A comparison of C/O in ratios between source and ambient particulate matter will show whether or not the formation of oxygenated-organic particulate matter is significant in the troposphere.

An oxygen thermogram of a portion of the material extracted from UCR-1 (Table 1) is shown in Fig. 3. This thermogram shows several notable features. There

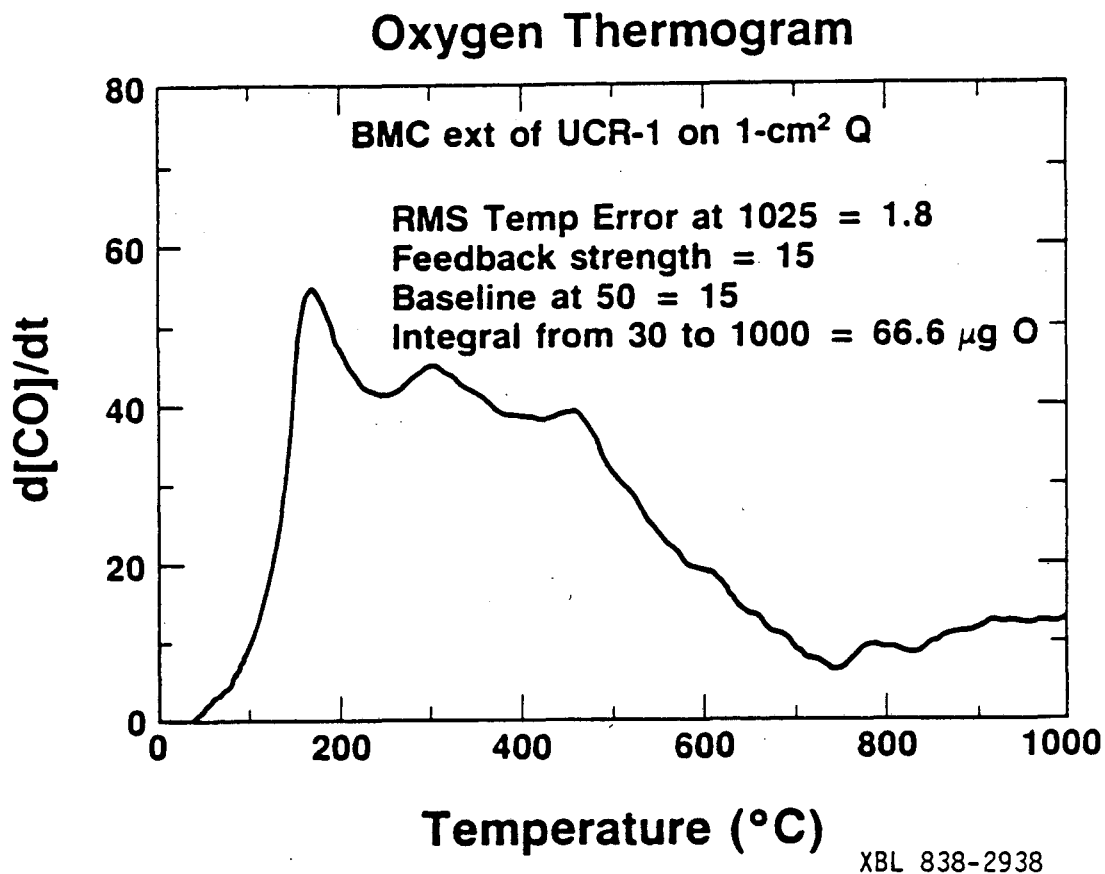


Fig. 3. Oxygen thermogram of a benzene/methanol-chloroform extract of a filter sample from Riverside, California.

is relatively little low-temperature volatile organic oxygen; and although the choice of a low-temperature interval is subjective, only a small fraction of O_p is evolved below 150°C . The thermogram shows that several dominant types of oxygenated material could exist in the sample, each having a characteristic temperature interval in which it evolves. The rising signal observed above 740°C is thought to be due to the decomposition of oxygen in organic material that carbonized during analysis — a plausible conclusion in light of char formation during analysis.

CONCLUSIONS

A technique has been developed that is sensitive enough to detect pyrolyzable oxygen in ambient particulate matter. The technique can be used to quantitate organic oxygen in solvent extracts of ambient particulate matter. Oxygen thermograms show distinguishable features that could be used to characterize general types of oxygenated material in ambient particulate matter.

ACKNOWLEDGMENT

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