Table I. Oxygen in standard compounds

Sample	Sample Type[a]	Detector[d]	Sample wt (μgO)	μgO Recovered (blank corrected)[b]	% Recovery $\bar{x} \pm s$ (n)	Deviation[c] (μgO)	Ave Deviation $\bar{x} \pm s$
Ammonium nitrate	S	C	612.6	605.0	99.0 ± 0.3	7.6	
			406.0	402.8	(2)	3.2	
Ammonium sulfate	W	N	7.1	6.8		0.3	
			14.3	15.1		0.8	
			14.3	14.6		0.3	
			28.6	29.0	99.8 ±3.8[e]	0.4	0.7 ± 0.5
			35.7	34.9	(7)	0.8	
			35.7	33.9		1.8	
			35.7	36.1		0.4	
Anthracene	S	C	1216.	7.2	0.6 ± 0.1	—	
			1517.	10.4	(2)	—	
Benzaldehyde 2,4-dihydroxy	S	C	318.0	343.4	108.1 ± 0.1	25.4	25.6 ± 0.4
			318.7	344.6	(2)	25.9	
Benzene, p-deithoxy	S	C	304.8	305.1	101.9 ± 2.5	0.3	5.1 ± 6.7
			268.4	278.2	(2)	9.8	
Benzoic acid	S	C	413.3	427.5		14.2	
			406.4	424.5		18.1	
			319.9	330.9		11.0	
			322.7	331.1		8.4	
			198.9	196.4		2.5	
			140.9	150.3	103.0 ± 3.7	9.4	10.7 ± 7.9
			316.8	325.8	(12)	9.0	
			155.8	160.6		4.8	
			240.5	255.8		15.3	
			322.8	352.4		29.6	
			103.5	98.5		5.0	
			177.5	178.5		1.0	
Benzoic acid, m-hydroxy	S	C	316.7	319.1	100.8 ± 0.1	2.4	2.3 ± 0.1
			252.7	254.9	(2)	2.2	
Blank boat (for weighed standards)		C	0	31.4			
			0	23.0			
			0	28.3			
			0	22.6			
			0	27.4	26.1 ± 2.9		
			0	22.6	(10)		
			0	26.2			
			0	25.4			
			0	28.2			
			0	25.5			
Blank boat + 1 cm^2 disc of quartz filter blanks		N	0	6.2			
			0	7.4			
			0	7.1			
			0	6.4	6.9 ± 0.4		
			0	7.2	(7)		
			0	6.9			
			0	7.0			
CO_2[f]	G	C	653.1	644.8		8.3	
				651.7		1.4	
				678.1		25.0	
				672.5		19.4	
				671.2	100.4 ± 2.3	18.1	13.1 ± 7.0
				668.8	(10)	15.7	
				638.9		14.2	
				644.0		9.1	
				646.9		6.2	
				639.2		13.9	

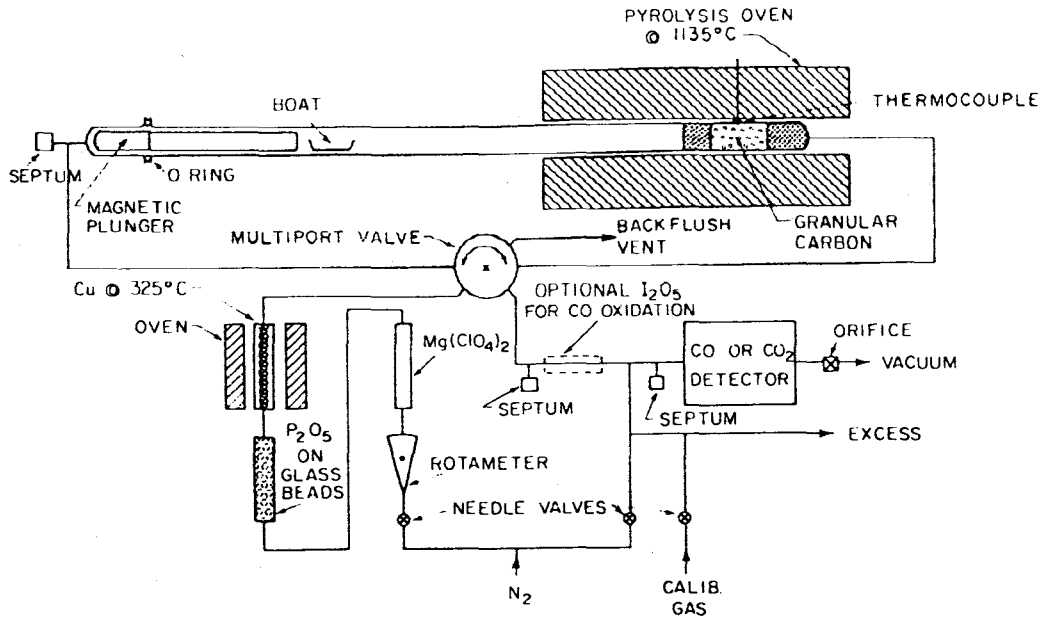

Figure 1. Schematic drawing of oxygen analysis system.

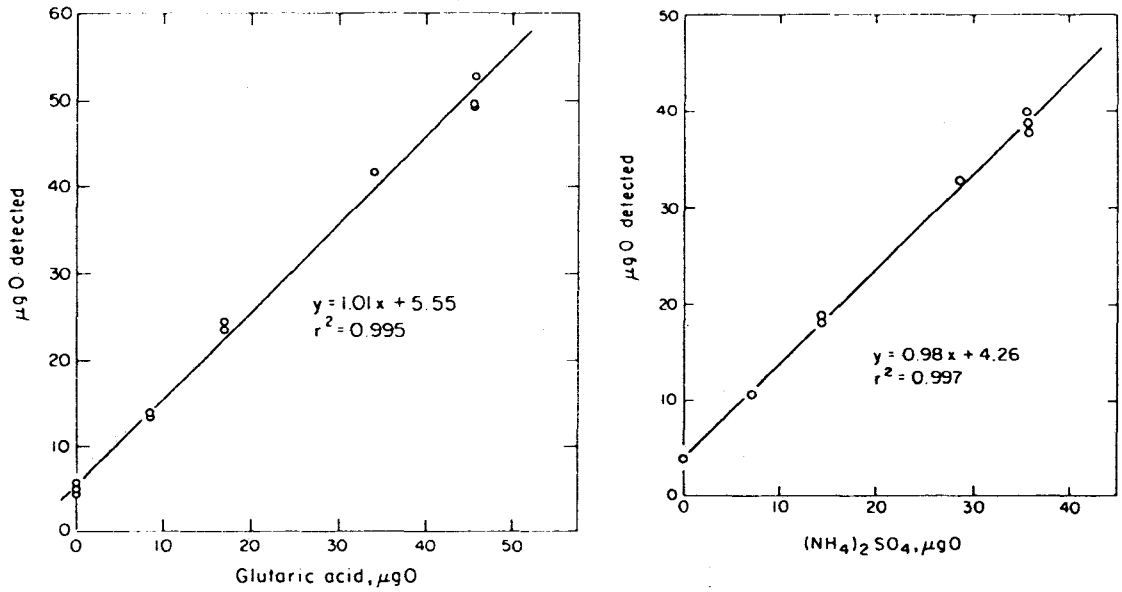

Figure 2. Recovery of oxygen in glutaric acid standard and $(NH_4)_2SO_4$ standard.

ambient particulate matter. The compounds presented in Table I have a variety of oxygen functional groups, some of which have been observed in ambient air and smog-chamber samples (*11*, *12*). The recovery of oxygen for each of these compounds is shown in Table I, and the overall results (percent recovery, average deviation, etc.) are summarized in Table II. The recovery for all standards was 101.4 ± 4.1% (n = 65). For standards analyzed with the coulometer, recovery was 101.2 ± 3.9% (n = 43), and recovery was 101.8 ± 4.5% (n = 22) for standards analyzed with NDIR detection. The analytical limits of detection (LOD) and LOQ were calculated according to American Chemical Society recommendations (*13*), as shown in Table II. Either of the detectors is suitable for analyzing oxygen in ambient particulate matter, but the NDIR system is probably more appropriate because of the low concentrations of oxygen expected on an air-filter sample.

A few comments should be made about preparation of low-concentration oxygen standards and their analysis. Benzoic acid was suggested as a reliable standard for this type of analysis (*14*) because it is available commercially in a primary standard grade. Our experience has been that only fresh primary standard benzoic acid gave results 100% of the expected value. For example, primary standard benzoic acid

Table II. Summary of Analyses of Oxygen Standards

	overall recovery		
detector	% recovery ± σ (n)	av dev[a]	sample size range
coulometer	101.2 ± 3.9 (43)	10.7 μg of O	101–678 μg of O
NDIR	101.8 ± 4.5 (22)	0.9 μg of O	7.1–45.6 μg of O
overall	101.4 ± 4.1 (65)		

Limits of Detection = Blank + $3\sigma_{blank}$

coulometer: 26.1 + 3 (2.9) = 34.8 μg of O
NDIR: 6.9 + 3 (0.4) = 8.1 μg of O

Limits of Quantitation = Blank + $10\sigma_{blank}$

coulometer: 26.1 + 10 (2.9) = 55.1 μg of O
NDIR: 6.9 + 10 (0.4) = 10.9 μg of O

[a] av dev = $(1/n)\sum_i^n$|expected − recovered|/expected.

Table III. Analysis of Filtered Ambient Particulate Matter

sample	time	date	μg of O/cm²[a]	μg of O/m³	μg of C/cm²	μg of C/m³
Berkeley, CA	1000-1715 h	11 March 1981	20.9	16.8	13.7	11.0
Berkeley, CA	1000-1715 h	11 March 1981	20.6			
Berkeley, CA	1000-1715 h	11 March 1981	20.9			
Berkeley, CA	1000-1715 h	11 March 1981	20.2			
Berkeley, CA	1800-0600 h	11-12 March 1981	21.0	[illegible]	12.9	[illegible]
Berkeley, CA	1800-0600 h	11-12 March 1981	20.8			

[a] Blank-corrected results.

ment on a laboratory shelf since 1953 gave results about 22.5 high, while fresh primary standard benzoic acid gave results as presented in Table I; however, the fresh benzoic acid sublimed to give 110-115% values around 1 year after purchase. Preparation of standards containing a few micrograms of O from benzoic acid is complicated because of its tendency to sublime. Gentle heating or evaporation caused losses of benzoic acid. Primary standard KHP or Na_2CO_3 is also a good standard because samples, if prepared from aqueous solutions, can be baked dry. But salts like KHP and Na_2CO_3 volatilize when placed in the pyrolysis tube, and the K or Na slowly devitrifies the hot quartz so that it becomes translucent and cracks. Therefore, KHP and Na salts are not standards of choice for this pyrolysis tube technique. Ammonium sulfate is available as a primary standard for N analysis and appears to be a good choice for an oxygen standard. Aqueous solutions of $(NH_4)_2SO_4$ can be evaporated onto disks of quartz-fiber filter material at 110 °C without decomposition. Heating circumvents the need for overnight desiccation that is required to dry aqueous solutions of organic oxygen compounds. Organic solvents could be used to prepare standards of organic oxygen compounds, but several organic acids we tried were not soluble in nonoxygenated solvents. Evaporation of oxygenated solvents on quartz-fiber filters always increased the blank value due to either incomplete evaporation or the presence of contaminants. Some variability in analysis was introduced during evaporation of low-level oxygen standards because calibration injections of CO_2 (Table I, NDIR detector) could be analyzed with $\sigma = \pm0.4\%$, while evaporated solutions of $(NH_4)_2SO_4$, KHP, and glutaric acid showed larger deviations ($\sigma = \pm2.5\%$, $\pm4.0\%$, $\pm3.7\%$, respectively).

Figure 2 shows the linearity and the scatter that can be expected for the analysis of standards prepared by the evaporation of solutions onto 1-cm² quartz-fiber disks. Each point is the determination of oxygen on a 1-cm² disk.

Replicate analyses of two ambient air filter samples are presented in Table III to show the applicability of this technique. A high-volume filter sampler (~1100 L min⁻¹ of ambient air was drawn through 400-cm² prefired quartz-fiber filters for several hours) was used to collect samples in Berkeley, CA. Multiple 1-cm² disks of these filters were desiccated for 12 h over P_2O_5 and then analyzed for oxygen. A separate technique (15) was used to analyze for particulate carbon. The results indicate that the volumetric flow rates frequently used to sample ambient particulate matter will collect enough oxygenated particulate matter so that 1 cm² of filter will give a signal above the LOQ in the NDIR analysis scheme. Comparison of the carbon loadings in Table III to Table II in Novakov (16) indicates that these loadings are typical for many United States sampling sites.

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