man, which makes the ocean by far the largest natural source of carbon monoxide known, if one assumes a worldwide production of carbon monoxide in the upper layers of the ocean similar to that found in the western Atlantic.

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3 October 1969; revised 1 December 1969

Airborne Lead and Carbon Monoxide at 45th Street, New York City

Abstract. *Daily business-day traffic determines the diurnal lead concentration as well as diurnal carbon monoxide concentration. Daily averages of 7.5 micrograms per cubic meter for lead and 13 parts per million of carbon monoxide were found for the 10-week period of the study. Correlations were demonstrated for lead and traffic and lead and carbon monoxide.*

The Department of Air Resources of the City of New York has initiated a program to monitor the lead content of the city's air. This effort is part of a larger monitoring program that includes the analyses of 12 metals collected at 38 sampling sites (New York City's Aerometric Network).

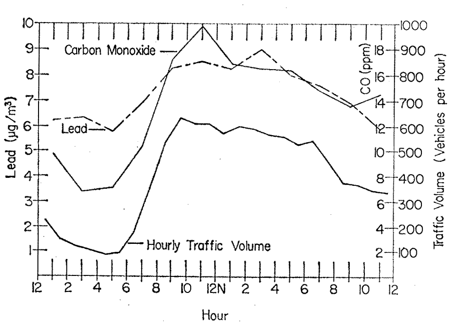

Fig. 1. Two-hour average lead concentrations in grams per cubic meter, carbon monoxide in parts per million, and hourly average traffic in vehicles per hour at East 45th Street, New York City.

This report includes lead concentrations at 6 m above street level at 110 East 45th Street and lead concentrations at two other elevated sampling sites in Manhattan—the Central Park Arsenal Building (Fifth Avenue and 64th Street) and at 240 Second Avenue. The sampling probes at the Central Park Arsenal Building and at 240 Second Avenue were located at an approximate height of 14 and 30 m, respectively. The 45th Street data represent the lead levels collected during a 10-week period from 12 January to 22 March 1969. Additionally, carbon monoxide readings are included for the same 10-week period for the 45th Street site. The lead was monitored by a sequential tape sampler. Two-hour spots were collected at 0.007 m^3/min with Whatman No. 4 tape. The carbon monoxide was measured with nondispersive infrared analyzer. The concentrations of lead and carbon monoxide are reported in micrograms per cubic meter and parts per million, respectively.

A previous study (*1*) at the 45th Street site showed this section of the city to be high in traffic volume and carbon monoxide pollution.

Equipment capable of collecting 2-hour sequential lead samples and continually monitoring for carbon monoxide concentrations was already present at 45th Street as part of a continuing effort by this department. The sampling probe for lead was located at approximately 6 m above street level and 2.6 m in from the curb. The carbon monoxide sampling probe was located approximately 6 m above street level and 3 m in from the curb. Lead samples were collected from the air over 2-hour periods, 24 hours per day, 7 days per week. The carbon monoxide concentrations were continuously monitored, 24 hours per day, 7 days per week. The average 2-hour concentrations of lead and carbon monoxide for the 10-week period between the hours of 8:00 a.m. and 6:00 p.m. were 9.3 $\mu g/m^3$ and 18 ppm, respectively. The carbon monoxide results are compatible with the previously reported results for 45th Street where the earlier investigators reported that the average hourly concentrations exceeded 15 ppm from 9:00 a.m. to 7:00 p.m. The carbon monoxide in both studies exceeded New York State's proposed standards.

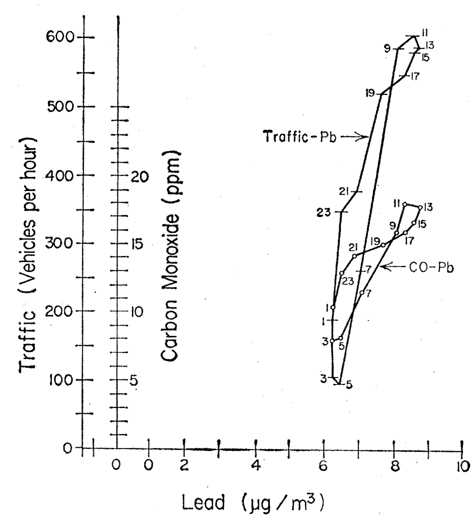

Fig. 2. Lead concentrations, traffic volume and lead concentrations, and carbon monoxide concentration curves at East 45th Street, New York City.

The means of the daily averages were 7.5 $\mu g/m^3$ for lead and 13 ppm of carbon monoxide for the 10-week period of the study. Similar results were reported (*2*) in another New York City study (on Broadway between 34th and 35th Streets). Here the authors reported an annual average for lead of 7.9 $\mu g/m^3$.

The frequency distribution for lead concentrations in the 2-hour samples (812 samples in milligrams per cubic meter), grouped in class intervals of 0 to 4.4, 4.5 to 8.4, 8.5 to 12.4, 12.5 to 16.4, and 16.5 to 20.4, was 32, 35, 16, 9, and 4 percent, respectively. During this same period, eight 2-hour readings were reported between 20.5 and

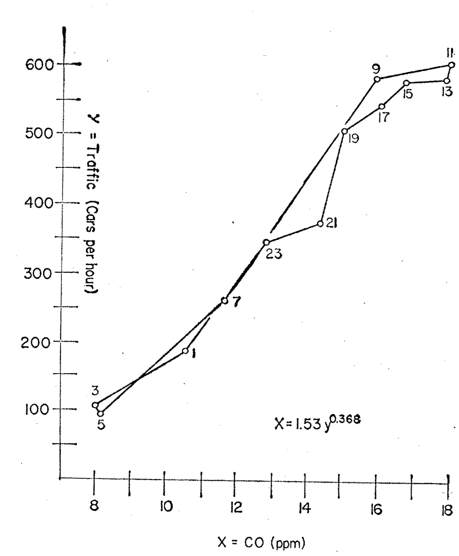

Fig. 3. Carbon monoxide concentration and traffic volume curves at East 45th Street, New York City.

24.4 $\mu g/m^3$, six between 25.5 and 28.4, two between 28.5 and 32.4, and one greater than 34.

When the lead and carbon monoxide concentrations were plotted against time the curves were similar in shape. These results are shown in Fig. 1. Both pollutants show peak values at 11:00 a.m. and later at 3:00 p.m. Plots of traffic volumes typical of 1967 at 45th Street correlate excellently with the pollutant plots (Fig. 1); this would indicate fixed traffic volume for 45th Street.

We smoothed the curves by calculating moving averages for carbon monoxide, lead concentrations, and traffic volumes. We then plotted the resulting moving averages—lead concentrations against carbon monoxide concentrations and traffic volumes (eliminating time). The results produced closed curves reminiscent of Lissajous figures (Fig. 2), thereby reinforcing the idea that correlations exist between lead and carbon monoxide and lead and traffic. Two other studies (*2, 3*) also report correlation between lead and carbon monoxide. The same graph of carbon monoxide plotted against the 1967 traffic count showed that carbon monoxide was a function of traffic (Fig. 3); it can be described by the equation $x = 1.53y^{0.368}$ (x = carbon monoxide in parts per million, and y = traffic in vehicles per hour).

We determined lead concentrations at Central Park (12-m elevation) and 240 Second Avenue (30-m elevation) for a 10-day period during the interval 23 January 1969 through 12 March 1969. The daily average for Central Park for this period was 0.97 $\mu g/m^3$; for Second Avenue the concentration for the same period was 1.57 $\mu g/m^3$. In another recent New York City study (*4*) the investigation reported annual mean lead concentrations of 3.82 and 2.99 $\mu g/m^3$ for the Bronx and Manhattan, respectively.

Similar lead concentrations were found at other elevated monitoring sites connected with the Aerometric Network. These lower values at rooftop sites suggest the need for a vertical profile for lead. This work is now in progress, and, in addition, lead concentrations are to be monitored at other sites of high traffic volume in New York.

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5 September 1969; revised 31 December 1969

Potassium Ion Specific Electrode with High Selectivity for Potassium over Sodium

Abstract. *A new potassium electrode, made from valinomycin, which uses commercially available electrode configurations, responds to potassium ion concentrations from 1 mole per liter to below 10^{-6} mole per liter. It is highly selective for potassium ion over sodium ion and divalent ions and can be used for the direct determination of potassium ion in human serum. No significant complexing of potassium appears to occur in normal serum.*

Measurements of the activities of the potassium ion are fundamental to an extremely wide range of problems, from membrane transport and nerve conduction processes to the potassium budget of the ocean. Until now the only really usable electrodes for potassium have been made from glasses, such as those first suggested by Eisenman and his colleagues (*1*); these electrodes typically [$NAS_{27\text{-}4}$ glass (27 mole percent Na_2O, 4 mole percent Al_2O_3, 69 mole percent SiO_2)] have a selectivity ratio of only 5 : 1 or 10 : 1 for potassium over sodium. Unfortunately, in many of the most interesting biological and geochemical applications, measurements have to be made in the presence of large amounts of Na^+.

A number of antibiotics, including valinomycin, the macrotetrolide actins, and the enniatins, have the ability to strongly affect K^+ transport in mitochondria (*2*); Stefanac and Simon reported (*3*) that the actin homologs dissolved in carbon tetrachloride or benzene could be used to make electrodes which were selective to K^+ over Na^+. They reported a selectivity of 750 : 1, but this was based on a slope of only 32 mv per decade change in activity derived from a plot of electrode response as a function of K^+ activity (the theoretical Nernstian response would be 59.6 mv). Pioda and Simon (*4*) reported that a plot of the electrode response of a suspension of nonactin in Nujol-octanol gave slopes approximately equal to theoretical values for K^+ concentrations between $10^{-1}M$ and $10^{-3}M$ and had a selectivity of approximately 100 : 1. Simon (*5*) reported that valinomycin gave a selectivity of 5000 : 1 for K^+ over Na^+ and a "linear response" between $10^{-1}M$ and $10^{-5}M$.

We report here a new electrode made with commercially available materials, which has a selectivity of better than 10,000 : 1 for K^+ over Na^+ and which can be used for the direct measurement of K^+ in serum. Using commercially available valinomycin (Calbiochem, Los Angeles, California, catalog No. 676377) without further purification, and a variety of aromatic solvents (such as nitrobenzene and higher homologs, diphenylether, chlorobenzene, or bromobenzene), we have prepared 5 percent to 10 percent (by weight) valinomycin solutions; we have used the solution as the "liquid ion exchanger" in a liquid membrane electrode body (Orion 92-Series electrode bodies). A double-junction reference electrode with 5*M* lithium trichloroacetate in the outer sleeve effectively prevented contamination of the solutions by K^+.

The response of a typical electrode to pure KCl solutions is shown by the solid line in Fig. 1, which is a plot of electrode response in millivolts as

Table 1. Comparison of measurements by flame photometer and electrode of concentrations (in millimoles per liter) of K^+ in serum samples.

Sample No.	Flame	Electrode	Recheck	
			Electrode	Flame
9788	4.1	4.5	4.5	4.5
9846	4.3	4.3	4.2_5	
9803	5.1	5.0	5.0_5	
9813	4.0	4.0	3.9	
9897	4.0	4.0	4.0_5	
9886	4.2	4.2	4.1_5	
9872	4.5	4.4	4.4	
9874	4.0	4.0	4.0	
9830	4.6	4.6	4.6	
9868	4.5	4.5	4.5_5	
9866	5.7	5.7	5.7	