

Radiocarbon Tracer Measurements of Atmospheric Hydroxyl Radical Concentrations

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Abstract. Radiochemical techniques have many untapped applications in atmospheric chemistry, especially when great sensitivity is required. We describe the application of these techniques to the measurement of hydroxyl radical concentrations in the troposphere.

Key words. Radicals, hydroxyl, tropospheric chemistry, radiochemical techniques, chemical measurements.

1. Introduction

Radiochemical methods have been widely used in biochemistry and other areas where it is necessary to quantitate accurately small quantities of material. So far, there has been little application of the technique to atmospheric chemistry despite the similarities of the problems to those confronting biochemists. The measuring of reactive radical concentrations in atmosphere is a good, if perhaps extreme, example of the problems of atmospheric analytical chemistry. The hydroxyl radical, at concentrations of 10^5 to 10^7 cm^{-3} in surface air and with a chemical lifetime of typically 0.1 s, has long defied easy measurement, notwithstanding the importance of its quantitation (Hoell, 1984).

Some years ago we were impressed by the sensitivity of techniques for quantitating carbon-14 compounds. These techniques have been highly developed by the carbon-14 dating community (Sheppard, 1975) and one of us (JCS) has been operating a carbon-dating facility for archeological and geological samples. Using heavily shielded gas proportional counters with anticoincidence discrimination against cosmic rays, a background of less than 1 count/min (cpm) at a counting efficiency of $(85 \pm 1)\%$ is attained. The uncertainty in this background is less than 0.03 cpm (standard deviation, SD). With a low-level sample counted for 6 h the sample activity can be determined to an uncertainty of 0.061 cpm (SD), corresponding to 5.16×10^{-16} mole or 3.1×10^8 molecules. These may be considered detection limits for carbon-14 labeled species, or for compounds

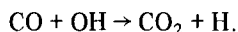
which can be quantitatively converted into carbon-14 species. Such detection limits are comparable to the best achievable by mass spectrometry and far lower than those attained by any other techniques commonly used in atmospheric chemistry, with the notable exception of electron capture gas chromatography. Similar, and in many cases lower, detection limits may be achieved using radiochemical methods with isotopes other than carbon-14.

The other approach to the measurement of atmospheric OH concentrations has been basically spectroscopic, typified by the laser-induced fluorescence methods developed by Wang *et al.* (1974) and Davis *et al.* (1976), and the direct absorption measurements of Perner *et al.* (1976). The radiochemical technique was first described in Campbell *et al.* (1979). Regardless of the method employed, OH signals are very small and the detection systems must be sensitive, instrumentally stable, and have the capacity to discriminate against external noise, physical and chemical. Furthermore, critical parameters, such as absorption coefficients or rate constants should be insensitive to changes in environmental factors. The subject is reviewed in Hoell (1984).

Ten years of laser-spectroscopic OH measurements have been characterized by attempts to use signal averaging techniques to extract vanishingly small signals from highly variable backgrounds (Wang *et al.*, 1981; Perner *et al.*, 1976; Hübler *et al.*, 1984; Davis *et al.*, 1979). Presently, the laser-spectroscopic methods, in spite of these efforts, can only yield lower limits of the OH concentration in the troposphere. The radiochemical method developed by Campbell *et al.* (1979) has yielded only slightly better results. In the following sections we outline attempts to use a ^{14}C tracer method and low level gas proportional techniques to measure tropospheric OH concentrations, and describe the development of techniques applicable to other gas-phase radioisotope studies of atmospheric chemistry.

2. Basis of the Radiochemical Method

The method we chose for converting OH concentrations to ^{14}C counting rates makes use of the deduction from studies of possible oxidants of CO that atmospheric oxidation of CO is dominated by OH via the reaction



This assumption is characteristic of all models (e.g., Logan *et al.*, 1981). We therefore add small quantities of ^{14}CO to the air being assayed for OH and collect the product $^{14}\text{CO}_2$, after an appropriate reaction time, for physical separation and quantitation by proportional counting. The ambient concentration of $^{14}\text{CO}_2$ is very low, about 10^4 cm^{-3} , and negligible relative to the added ^{14}CO . The principal precautions required are concerned with minimizing the loss of radicals to the structure of the apparatus and the ensuring of rapid and thorough mixing of the added ^{14}CO tracer into the sampled air. The detection limit is determined by the efficiency of the purification of the ^{14}CO before the reaction and the separation of ^{14}CO from $^{14}\text{CO}_2$ after the reaction, by spurious (usually surface catalytic) oxidations which compete with the OH radical oxidation, as

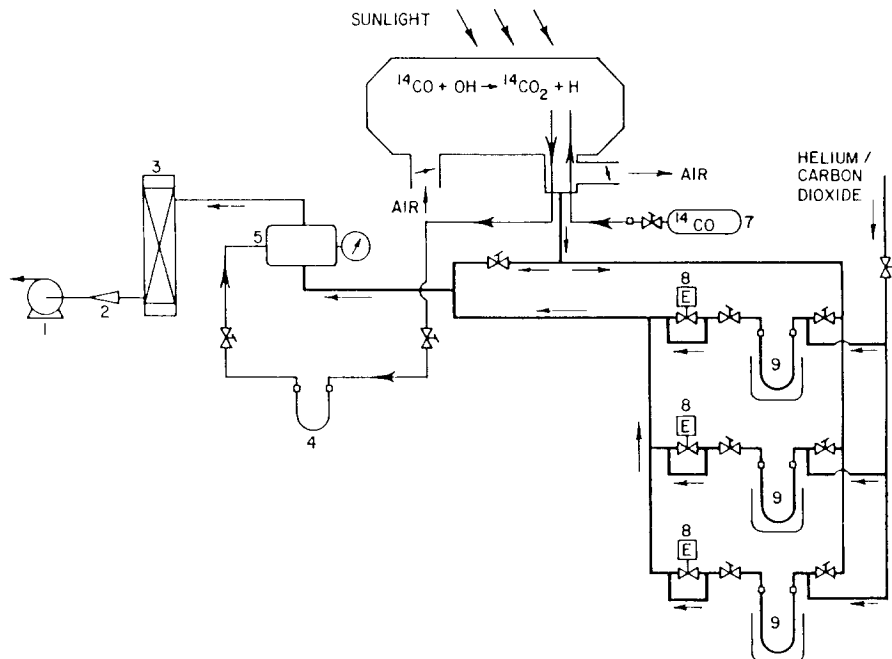


Fig. 1. Flow paths of WSU static OH reactor. (1) pump; (2) exhaust line; (3) Ascarite absorbent; (4) ^{14}CO assay loop; (5) Hopcalite catalyst to oxidize ^{14}CO ; (6) UV-transparent Teflon[®] reaction vessel, volume about 100 l; (7) ^{14}CO storage vessel/injector; (8) solenoid valves used with liquid nitrogen-cooled freeze-out loops (9) to collect $^{14}\text{CO}_2$ formed by OH oxidation of ^{14}CO in reactor (6). The $^{14}\text{CO}_2$ was further purified and gas proportional counted.

well as by the minimum detectable quantity of ^{14}C discussed above.

Over the past 8 yr we have used three variations of this method, which will be described and analyzed as steps in an evolutionary process. The techniques have obvious applications in areas of atmospheric chemistry other than hydroxyl measurement.

3. The Teflon Bag Static Reactor

In this variant the ^{14}CO oxidation rate is measured in an air sample which as far as possible approximates its original photostationary state in a static enclosure. Details of the apparatus are shown in Figure 1. High specific activity (60 Ci/mole) and very high purity are needed in the ^{14}CO tracer, with $Q = [^{14}\text{CO}]/[^{14}\text{CO}_2]$ ratios of $> 10^5$. The ^{14}CO was initially made by the dehydration of ^{14}C -formic acid with concentrated sulfuric acid and the removal of residual $^{14}\text{CO}_2$ with liquid nitrogen traps. Subsequently, the need for higher purity ratios ($Q > 10^8$) for the quartz flow reactor led to the use of zinc reduction of $^{14}\text{CO}_2$ at 400° with more comprehensive cryogenic purification (Hardy *et al.*, 1984) and its employment in subsequent measurements (Sheppard *et al.*, 1982). Tests of the new ^{14}CO preparation method (Farmer *et al.*, 1985) routinely yielded purity ratios between 10^8 and 10^9 .

The purified ^{14}CO tracer in quantities of 0.25 mCi (10^7 Beq) was pressurized to 20

atm with helium in stainless steel vessels. Immediately before each measurement, a portion was passed through a cryogenic liquid nitrogen trap to remove $^{14}\text{CO}_2$ catalytically- and radiolytically-produced during storage. Measurements by Hardy *et al.* (1984) confirmed that the ^{14}CO radiolyzes to $^{14}\text{CO}_2$ with a rate constant of 10^{-5} hr^{-1} (Anderson *et al.*, 1966; Dondes *et al.*, 1964; Clay *et al.*, 1963) and a similar rate of catalytic oxidation occurs under the storage conditions. The repurified tracer was stored in a previously evacuated vessel pressurized to 7 atm prior to injection into the reaction chamber.

The chamber is fabricated from 0.05 mm UV inhibitor- and plastizer-free FEP Teflon film which absorbs less than 5% of the incident photolytic light; the film is handled only with gloves and is changed every few runs. Prior to the measurement the chamber is continuously flushed with the air to be sampled; valves are then closed to isolate the chamber contents and the ^{14}CO tracer is rapidly mixed with the confined air. At pre-selected reaction times, ranging between 10 and 100 s, solenoid valves are opened to remove aliquots of a few filters from the center of the reaction chamber; these samples are passed through traps at liquid nitrogen temperature to remove the $^{14}\text{CO}_2$ from the unreacted ^{14}CO . The loops, still at liquid nitrogen temperature, are then flushed with a helium/carbon dioxide mixture to remove most of the residual ^{14}CO and returned to the laboratory for further purification. Subsequent deposition and sublimation remove ^{14}CO down to less than 10^{-6} of the original quantity passing through the freeze-out loops. The purified $^{14}\text{CO}_2$ is transferred to a gas-proportional counting tube and counted for times sufficient to obtain a precision of 3%. Tests indicate a $(50 \pm 15)\%$ recovery of $^{14}\text{CO}_2$. The ^{14}CO concentration in the reaction chamber is determined by taking several 6.3 cm^3 aliquots of the chamber's contents for gas proportional counting. The reproducibility of these samples is about 5%.

Each measurement is corrected for collection and counting efficiency. A least-square regression of the $[^{14}\text{CO}_2]/[^{14}\text{CO}]$ ratios versus time yields a slope equal to $k[\text{OH}]$, from which the OH concentration is calculated using a rate constant of $2.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (Baulch *et al.*, 1980; Ravishankara and Thompson, 1983; Paraskevopoulous and Irwin, 1984). The results are reported in Table I. The regression analysis of many measurements, each with 3 to 4 successive reaction times, showed coefficients of determination, r^2 , greater than 0.8, with outliers attributed to radiolytic ^{14}C surface contamination, variations in $^{14}\text{CO}_2$ recoveries, and wall effects.

4. Discussion of Static Reactor

The static chamber measurements were not without their the limitations, discussed below, but are important as proofs of the principle. Two distinct approaches confirmed that a photochemical reaction was measured. Numerous blank measurements were performed in the dark and showed no significant oxidation of ^{14}CO to $^{14}\text{CO}_2$ even over periods of 20 to 30 min, several times the normal run duration. In addition, experiments performed in Antarctica by Sheppard *et al.* (1982) yielded results consistent with OH concentrations of less than $2 \times 10^5 \text{ cm}^{-3}$. These establish a detection limit of approximately 10^5 cm^{-3} .

Wall losses constitute the principal bias of the static technique. Both the OH and HO_2

Table I. Measured hydroxyl concentrations and ancillary data

Measurement	[OH] 10 ⁶ cm ⁻³	Quality*	J(O ¹ D) 10 ⁵ s ⁻¹	mr(O ₃) ppb	p(H ₂ O) Torr	sec θ [†]
WSU12 ¹	2.5	1	2.95	46	23.2	1.14
WSU13	4.2	1	2.44	35	—	1.25
WSU14	6.1	1	2.55	32	7.44	1.25
WSU15	4.6	1	2.78	63	—	1.19
WSU16	7.1	1	2.73	32	6.60	1.30
WSU17	6.8	3	2.48	24	6.60	1.45
WSU18	3.1	1	2.87	32	7.72	1.30
WSU19	9.7	2	2.34	14	7.01	1.66
WSU20	7.9	2	2.77	18	6.78	1.43
WSU22	24	1	2.31	18	6.98	1.33
WSU23	38	1	2.29	20	5.21	1.76
WSU24	12.9	1	2.63	20	5.21	1.48
WSU27	1.7	3	—	—	6.62	2.35
WSU34	5.4	1,4	—	—	5.46	1.51
NZ4 ²	0.8	3	1.28	34	7.70	1.82
NZ6	0.9	3	2.36	20	7.50	1.54
NZ8	1.6	3	1.15	23	8.50	2.10
TN2 ³	3.0	1	1.66	87	24.3	1.27
TN3 ⁴	1.5	2	2.20	28	31.3	1.27
TN4 ⁵	2.0	1	2.28	45	24.6	1.24
TN5	1.8	3	2.16	50	33.5	1.39
TN6	1.0	2	1.16	55	33.6	1.68
LA1 ⁶	6.2	1	2.34	170	9.24	1.15
LA4	3.7	2	2.09	320	14.45	1.37
LA5	5.2	2	1.18	270	13.45	1.79
AZ5 ⁷	37	3	5.44	44	2.51	1.47
AZ6	86	3	7.07	44	2.28	1.26
AZ8	64	3	9.22	49	2.07	1.06
AZ10	39	3	7.16	51	1.85	1.08
PR4 ⁸	4.0	3	—	—	39.2	1.08
PR5	2.0	3	—	—	40.5	1.04
BS1/2 ⁹	7.2	3	3.8	—	41.2	1.05
BS3	20	3	3.2	—	40.5	1.23
BS4/5	4.8	3	2.9	—	39.2	1.34
BS6	18	3	2.6	—	36.5	1.48
CO2/3 ¹⁰	4.2	3	3.1	40	24.3	1.27
CO5	1.7	3	3.5	53	30.3	1.15
MCM ¹¹	< 2.5 × 10 ⁵	2	0.092 ± 0.018	8.9 ± 0.3	2.5 ± 0.5	1.70
POL ¹²	< 3.1 × 10 ⁵	2	0.051 ± 0.01	7.1	0.3	2.56
Background ¹³	< 2 × 10 ⁵	—	—	—	—	—

¹ Pullman, Washington, 46.7° N, 117.2° W, 770 m altitude, July 1978. WSU13 to WSU15 performed 8–26 June 1979. WSU16–WSU18 performed 24–26 Aug. 1979. WSU19–WSU23 performed 7–17 Sept. 1979. WSU24 performed 1 Oct. 1979. WSU27 performed 1 Dec. 1979. WSU34 performed 5 Aug. 1980.

² Mt. John, New Zealand, 44.0° S, 170.5° E, 1030 m altitude, 2–6 April 1978.

³ Rural Tennessee, 36.5° N, 87.7° W, 180 m altitude, 13 Aug. 1978.

⁴ Rural Tennessee, 35.6° N, 86.5° W, 230 m altitude, 15 Aug. 1978.

⁵ Rural Alabama, 34.9° N, 85.7° W, 460 m altitude, 16 Aug. 1978.

⁶ Claremont, California, 34.1° N, 117.7° W, 270 m altitude, 1 Sept. 1978. Mr(NO₂) ~ 75 ppb,

Table I (continued)

(except LA1, ~130 ppb), $m_r(\text{NO}) = 0$.

⁷ Zilnez Mesa, Arizona, 36.8° N, 110.7° W, 2300 m altitude, 6–8 July 1979.

⁸ Cape San Juan, Puerto Rico, 18.4° N, 65.6° W, 30 m altitude, 12–13 May 1980.

⁹ Ragged Point, Barbados, 13.5° N, 59.0° W, 20 m altitude, 22 May 1980.

¹⁰ Pawnee Grasslands, Colorado, 39.4° N, 104.6° W, 1640 m altitude, 11 June 1980.

¹¹ McMurdo Station, Antarctica, 77.9° S, sealevel, 10–12 Jan. 1982, mean of four measurements, effectively determining the instrument's detection limit.

¹² South Pole, Antarctica, 90° S, ~2750 m altitude, 20 Jan. 1982, another determination of the detection limit, mean of three measurements.

¹³ Mean of eight background measurements done in darkness. Effectively these measurements indicated no ¹⁴C oxidation in the absence of sunlight and determined the instrument's detection limit.

* Quality assessed on basis of internal consistency of data:

1 = good, $r^2 > 0.8$

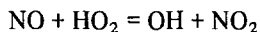
2 = fair, $r^2 < 0.8$ and > 0.5

3 = poor with evidence of particulate ¹⁴C contamination, $r^2 < 0.5$

4 = after decontamination to remove particulate ¹⁴C

† θ is the solar zenith angle

radicals must be considered because, for the long reaction times of the static system, the latter is also a significant contributor to the OH concentration via the



reaction. We have estimated OH and HO₂ wall losses by calculations similar to those of Lynch and Michael (1978). Calculations were performed for the full range of expected chemical lifetimes for both OH and HO₂ radicals, and for diffusion coefficients ranging from those measured in calm air up to those expected in windy environments, where motion of the chamber walls enhances diffusion. In all cases we assumed zero radical concentrations at the surface of the reactor, an unrealistically stringent condition since decomposition at the walls is not generally collision limited. Thus, the calculations overestimated wall losses of both radicals. The spatially averaged chamber OH concentration during the reaction time resulting from these calculations was 45% of that of the air being sampled in the worst case; for conditions more typical of those at our field sites it was about 80% of the ambient concentration.

5. The Flow Reactor

Although the wall interactions of the static measurements were not unreasonably large for a preliminary measurement (and compare well with the uncertainties specific to other techniques), they constituted an intractable limitation when errors of less than 20% are sought. To circumvent this difficulty we changed to a flow reactor with a much shorter reaction time, short enough that the central part of the flow in the reactor would not be in diffusive contact with the reactor walls. Construction and testing of this instrument began midway through the series of measurements described above.

The reactor consists of a quartz tube, transparent to all photolytic radiation, with a diameter of 20 cm and a length of 1 m. In use it is faced directly into the mean wind at a height of 2 m above the surface. Air flow as it enters the reactor entrance is not laminar

and inherits all the external turbulence with scales smaller than the tube's diameter, but this decays rapidly as the flow proceeds along the tube. Photographs of smoke entering the reactor indicated low mixing except from eddies with scales approaching the tube diameter and directed normal to its axis. Such eddies were infrequent and can be monitored if necessary.

Extensive wind tunnel testing and $K-\epsilon$ numerical modelling of the flow plus chemistry (Meyn, 1982) of inlet designs were done. The resulting design shows recirculation-free flow over a range of about 9° between the wind direction and the tube's axis. Wall losses or contamination of that part of the flow collected within 3 cm of the reactor's axis were shown to be negligible. The quartz walls permit the maintenance of the external photostationary state essentially unchanged, and without an initial depletion of radicals which occurred in the static reactor. The modelling also shows (Meyn, 1982) that the OH concentration in that part of the flow which is subsequently collected is uniform and $>98\%$ of the external concentration even if we assume the walls to be a perfect sink for all radicals. As shown in Figure 2, the reactor has a 30 cm front section to allow the decay of small-scale turbulence, followed by a 37-nozzle array that injects the ^{14}CO tracer into the air flow, where rapid mixing occurs. Radical destruction by the nozzles themselves is calculated to be less than 5% on the basis of 100% loss on contact; the integrated effect over the reactor length is typically severalfold smaller because of the recovery of concentration towards the photostationary state values as the air passes beyond the nozzles.

At the far end of the reactor the central 6% of the air flow is passed through an aluminum screen to remove radicals and define the reaction time. This air is passed through a water vapor trap, and the CO_2 collected in the liquid nitrogen-cooled cryocondenser (PCU) at about 100 K. To remove the codeposited ^{14}CO tracer and other impurities, the cryodeposit is sublimed and transferred to the secondary cryocondenser

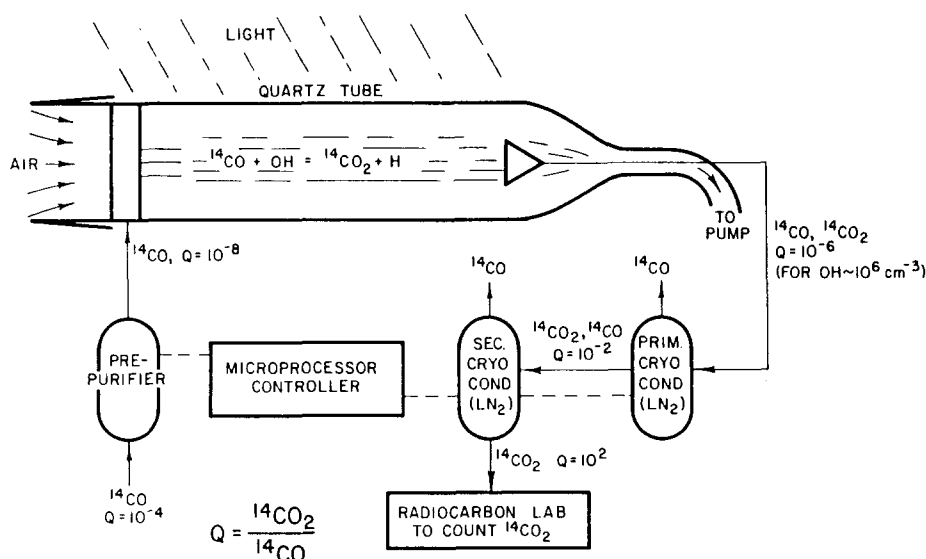


Fig. 2. Schematic of quartz tube flow reactor. Values of Q are for ideal operating conditions.

with a helium flush and redeposited. After further flushing it is sublimed and transferred to a 7 cm³ container in which it is returned to the laboratory for gas proportional counting. A small, time-averaged aliquot of the central air flow is collected to determine the initial ¹⁴CO concentration. The monitoring of temperatures, flows and pressures, and timing valves are microprocessor controlled to ensure reproducibility.

The reaction time in the flow reactor is set by the requirement that the central portion of the flow not be in diffusive contact with the walls. By this means the integrity of the sampled air is preserved at the expense of signal-to-noise ratio (SNR). At a reaction time of 8 s and an ambient OH concentration of 5 × 10⁴ cm⁻³, only 1.2 × 10⁻⁷ of the injected ¹⁴CO is converted to ¹⁴CO₂. Attaining a sufficient quantity of ¹⁴C to count is not difficult; the duration of the collection time need only be extended until the required quantity is collected. A reasonable run time of 100 s is adequate at a ¹⁴CO mixing ratio of 30 ppb, about 15% of the ambient (northern hemisphere) CO mixing ratio.

The major limitations on SNR arise from (a) ¹⁴CO₂ impurities in the ¹⁴CO tracer; (b) imperfect separation of ¹⁴CO from the ¹⁴CO₂ produced in the reaction; (c) catalytic and other spurious oxidation of ¹⁴CO to ¹⁴CO₂ during the run; and (d) ¹⁴C-labeled impurities (other than ¹⁴CO₂) in the ¹⁴CO tracer. Achieving an SNR of unity at an OH concentration of 5 × 10⁴ cm⁻³ requires that the background of apparent ¹⁴CO₂ contributed by all these effects have a standard deviation of less than 0.6 × 10⁻⁷, expressed as a fraction of the total quantity of ¹⁴CO injected.

Initial trials of the flow reactor showed a large background under conditions where the OH concentration was expected to be negligible. The cause proved to be catalytic oxidation of CO to CO₂. Stainless steel had been chosen as a catalytically inert material on the basis of its performance in gas chromatography columns. Measurements by Fitzner (1984) and Farmer *et al.* (1985) showed that stainless steel is an effective catalyst for CO oxidation, indeed almost as effective as copper and its oxides. Some aluminum alloys showed a very low catalytic oxidation rate, equivalent to an OH concentration of less than 10⁵ cm³. All critical units (tubing, nozzle assembly, collection cone, and the primary cryo-condenser) were then refabricated from aluminum alloys.

6. Reduction of the Flow Reactor Data

In contrast to the static reactor, the flow reactor has a fixed reaction time T , nominally 8 s. This time can be determined by numerical modelling or more directly by measurements of the time dependence of the concentration at the collection cone after a step-function increase in concentration of tracer emitted by the injectors. As mentioned, modelling show the OH concentration in the collected part of the flow to be uniform and essentially the external OH concentration. In the ideal case of immediate mixing of the ¹⁴CO into the full cross-section of the flow the kinetics reduce to a very simple form. Let $F(t)$ be the distribution of ¹⁴CO transit times between the injectors and collector. The concentration of ¹⁴CO₂ after a reaction time t is

$$\int_0^t k[\text{OH}][^{14}\text{CO}]dt \quad (1)$$

which reduces to kt $[\text{OH}][^{14}\text{CO}]$ for uniform OH and ^{14}CO concentrations over the path followed by the ^{14}CO molecule. The mean concentration of $^{14}\text{CO}_2$ at the collector is obtained by integrating over the transit time distribution,

$$\begin{aligned} [^{14}\text{CO}_2] &= \int_0^\infty ktF(t) [\text{OH}][^{14}\text{CO}] dt \\ &= k [\text{OH}][^{14}\text{CO}] \int_0^\infty t F(t) dt \\ &= kT [\text{OH}][^{14}\text{CO}] \end{aligned} \quad (2)$$

Here $T = \int_0^\infty t F(t) dt$ is the mean reaction time, which can be found by measuring the time dependence of the concentration of ^{14}CO at the collector after a step-function increase in concentration at the injectors. If the step is from zero to C at time $t = 0$, the concentration at the collector at time t is

$$\begin{aligned} c(t) &= \int_0^\infty C F(t - t') dt' \\ &= C \int_{-\infty}^t F(t') dt' \end{aligned} \quad (3)$$

from which $F(t)$ may be recovered by differentiation.

At OH concentrations well above the noise level the flow reactor is capable of measuring the rate of oxidation of CO to high accuracy without calibration by a source of radicals of predetermined concentration. Accuracies of better than $\pm 15\%$ appear obtainable with the largest uncertainties arising from variations in the efficiency of the cryocondensers, which are deliberately kept small in area to minimize catalytic oxidation. The OH concentration will have additional errors from the OH-CO reaction rate constant and from the expected very small contributions of methoxyl and other radicals to the oxidation.

The detection limit is determined by the stability of the background signal. More specifically, the noise level is the standard deviation of the ^{14}C count rate of samples obtained under conditions where the OH concentration is zero, expressed in terms of an equivalent OH concentration by means of the instrument calibration factor. In practice this background variance is dominated by effects of the ^{14}C impurities in the ^{14}CO tracer, and by inefficiencies in the separation of ^{14}CO from the desired $^{14}\text{CO}_2$ after the reaction. The counting background is very stable and contributes little to the variance; the ambient $^{14}\text{CO}_2$ concentration is low enough to contribute only marginally to the background and is expected to be stable.

7. The Wallops Island Tests

During July, 1983 in an intercomparison of hydroxyl measuring instruments organized by the National Aeronautics and Space Administration at Wallops Island, Virginia. The flow reactor was compared with two laser-induced fluorescence instruments developed by the Ford Motor Company Research Laboratories and Georgia Institute of Technology.

Details of this intercomparison are given elsewhere (Hoell *et al.*, 1984).

The flow instrument was completed only immediately before the Wallops Island intercomparisons. Initial background measurements (Table II) showed the background to be both large and unstable. This unexpected result was found to be due to use of new $^{14}\text{CO}_2$ stock material for preparation of the ^{14}CO tracer which upon analysis contained 3% $^{14}\text{CH}_4$ as a contaminant. Existing purification procedures were inadequate to remove $^{14}\text{CH}_4$ in this quantity. The problem was exacerbated by a failure of the microprocessor control system; manual operation caused the rejection of the $^{14}\text{CH}_4$ in the post-collection purification stages to be less predictable.

The Wallops Island data are summarized in Table II. Because of the variable background these data can only be interpreted as upper limits on the ambient hydroxyl concentration. The earlier measurements in the series appear to be less problematical. The data obtained by the LIF instruments were rarely above the noise level, but data which were acceptable and which coincided in time with the radiochemical measurements indicated general agreement; reference should be made to the detailed paper mentioned above.

Recent improvements to the flow instrument have included replacement of most of the remaining catalytically-active surfaces with inert materials, optimization of the processing system and more effective steps to remove $^{14}\text{CH}_4$ from the stock $^{14}\text{CO}_2$ before conversion to ^{14}CO . Further measurements will be reported shortly.

Table II. WSU data for Wallops Island OH measurements

Sample ID	Date July 83	Mean Time	Collection Time sec	T sec	NV 10^6 dpm	S dpm	[OH] ^a 10^6 cm^{-3}
GT 4	21	19 : 32 : 12 EDT	100	8.17	2.78	122.4	21.0 ^b
7	21	20 : 51 : 12	100	7.91	2.32	45.4	10.2
8	22	11 : 23 : 35	110	8.29	0.298	7.9	12.1
10	22	13 : 08 : 15	100	8.49	0.367	5.1	6.2
11	22	13 : 47 : 26	103	8.65	14.02	43.5	4.7
12	22	14 : 09 : 30	100	8.55	3.51	57.6	7.3
13	22	15 : 21 : 00	100	8.29	3.67	149.4	18.6 ^b
15	22	18 : 10 : 05	100	8.20	1.44	130.6	42.1 ^b
16	22	18 : 35 : 35	100	8.29	2.38	49.4	9.5 ^b
17	22	19 : 07 : 50	100	8.20	2.22	60.0	12.5 ^b
Background measurements at WSU							
BKG 2	19	20 : 30 PDT	100	8.12	16.4	24.7	1.4
4	19	22 : 30	90	8.2	1.5	18.0	2.3
5	20	00 : 30	100	8.21	3.8	5.1	1.3
6	20	2 : 00	100	8.24	7.4	0.54	0.068
7	20	2 : 30	100	8.2	5.4	1.67	0.44

^a Values reported are upper limits of the OH concentration.

^b $^{14}\text{CO}_2$ recovered in measurements 4 and 13 to 17 was contaminated with $^{14}\text{CH}_4$; see text for additional details. dpm: disintegrations min^{-1} . NV and S are the total added ^{14}CO and collected $^{14}\text{CO}_2$ in activity units.

8. The Aircraft OH Titration Reactor

Both the static and flow reactors are restricted to ground level or tower measurements but it is desirable to make OH measurements as a function of altitude, ideally in an aircraft. At the request of NASA, we attempted to build a modification of the flow reactor. It was considered impractical to decelerate the air to be sampled from the near-sonic velocity of the aircraft to the velocity of $\sim 10 \text{ cm s}^{-1}$ required for a photostationary reactor such as used for ground measurements. We therefore elected to use a high velocity reactor with a 0.2 s reaction time, with higher ^{14}CO concentrations, and with no attempt to preserve intact the atmospheric photochemistry. This required a fundamental alteration in reactor design; the operation may be thought of as titrating the atmospheric OH with ^{14}CO ; in practice we secure 5 to 30% conversion of ^{14}CO to $^{14}\text{CO}_2$. A reactor designed to fly in a NASA Convair 990 research aircraft and partially tested in that vehicle is described in the following sections.

Figure 3 shows the flow of air through the reactor and indicates methods for measuring them. Air is first decelerated by passage close to the stagnation point on an axisymmetric airfoil external to the aircraft. The air is slowed further by passage through a second quasi-stagnation region just inside the mouth of the inlet tube. At the second deceleration point the central air flows into the inlet, while the outer flow is reflected by the pressure gradient and forms an insulating reverse-flow region adjacent to the inside

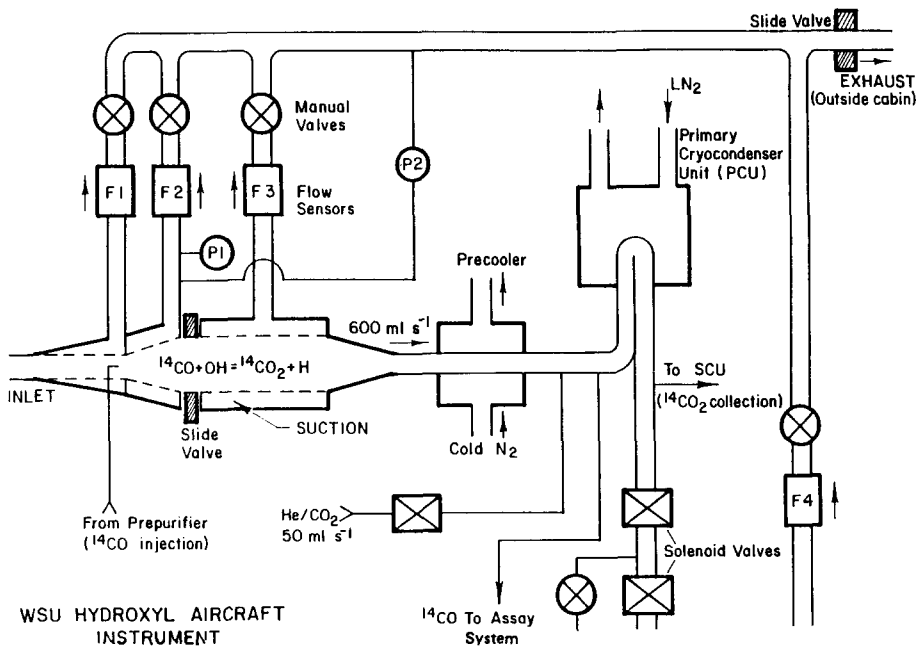


Fig. 3. Principal flow path of WSU airborne OH titration instrument. Air external to aircraft enters at inlet. $F1 = 4.7 \text{ l s}^{-1}$, $F2 = 0.8 \text{ l s}^{-1}$, $F3 = 2.4 \text{ l s}^{-1}$, and $F4 = 0.6 \text{ l s}^{-1}$.

wall of the inlet. These two decelerations reduce air velocity from about 250 m s^{-1} to 27.4 m s^{-1} . Because of short development times the boundary layers (i.e., the regions of the flow in which radicals are depleted) are very thin compared to the dimensions of the sample airstream; unless the flow is grossly turbulent, radical losses will be negligible.

Before the injection of the ^{14}CO tracer, the air flow is further decelerated by graded suction to a final velocity of 2.5 m s^{-1} in a porous-walled conduit and short diffuser. To determine wall losses the walls were coated with 2,4-dichlorophenoxy acetic acid isopropyl ester and its concentration measured in both the main flow and air sucked through the porous wall. The ratio of these is a measure of mass transfer from the wall to the main air flow and hence of radical losses to the walls; an upper bound radical loss of 4% was found in the laboratory. Corresponding measurements on the NASA CV 990 in flight showed losses of about 15% due to grossly turbulent flow at the stagnation point of the outer inlet caused by major misalignment of the external airfoil with respect to the air-flow outside the cabin.

The ^{14}CO tracer is injected into the flowing air with 4 nozzles of 0.1 mm tubing at the entrance to the diffuser section. The air then flows through a porous-walled reactor with graded suction where the mean velocity is reduced to 0.5 m s^{-1} ; the nominal reaction time is 0.22 s. A screen at the rear of the reactor quenches unreacted radicals and defines the reaction time.

Carbon dioxide emerging from the reactor is cryogenically separated from the unreacted ^{14}CO for subsequent low level proportional counting. As in the quartz flow reactor, all critical surfaces are made of aluminum to reduce catalytic oxidation of the ^{14}CO to a minimum. Separation ratios of 10^9 are required to detect the $^{14}\text{CO}_2$ produced by the OH oxidation of ^{14}CO ; these are achieved by passing the effluent from the reactor through a three stage deposition/sublimation unit. Tests have indicated that the desired purities and separation ratios can be obtained provided the ^{14}CO tracer is reasonably free of $^{14}\text{CH}_4$. Assay of the ^{14}CO concentration injected into the reactor is done in the same way as on the quartz flow reactor.

9. Reduction of the Aircraft Instrument Data

We begin by assuming that the air being sampled is in a photostationary state dominated by a concentration-independent source P_0 and a first-order loss term:

$$d[\text{OH}]/dt = P_0 - [\text{OH}]/\tau_0 = 0 \quad (4)$$

where τ_0 is the lifetime of the radical against loss under ambient conditions. P_0 can be considered the sum of a term P_p representing the promptly light-dependent sources of OH, that is, those which vanish in a time much less than τ_0 after the cessation of illumination, and a term P_d representing the other sources, such as conversion of HO_2 radicals. We write $P_d = fP_0$; models provide estimates of f which are typically less than 0.5 in clean air.

After the admixture of ^{14}CO Equation (2) will be modified to

$$d[\text{OH}]/dt = P_0 - [\text{OH}]/\tau_0 - k[^{14}\text{CO}][\text{OH}] \quad (5)$$

where k is the rate constant for the OH–CO reaction. This equation can be solved for [OH] as a function of time and we can calculate the concentration of $^{14}\text{CO}_2$ at the reactor exit after reaction time T :

$$[^{14}\text{CO}_2] = k\tau[^{14}\text{CO}][\text{OH}]_0(1 - f\tau/\tau_0)(1 - \exp(-T/\tau) + fT\tau/\tau_0) + [^{14}\text{CO}_2]_0 \quad (6)$$

where $[\text{OH}]_0$ is the ambient concentration, $[^{14}\text{CO}_2]_0$ is the background concentration in the absence of ambient OH, and $\tau = \tau_0/(1 + k\tau_0[^{14}\text{CO}])$.

Sensitivity analysis of Equation (6) shows generally weak dependence on poorly known quantities such as f and τ_0 ; typically, errors of 30% in either of these will result in an error of only 3% in [OH]. In this regard the aircraft technique is an acceptable replacement for the photostationary technique of the flow instrument and is capable of almost comparable accuracy. The price paid for the short reaction time shows up in the detection limit. From Equation (6) with optimum values of $[^{14}\text{CO}]$ one deduces that the fraction of labelled impurities in the ^{14}CO should not exceed 2×10^{-9} and separation ratios of 10^9 are required in the post-reaction processing. In this regard the $^{14}\text{CH}_4$ contamination of the stock $^{14}\text{CO}_2$ has turned out to be a major problem, and the development of a method to remove it did not occur in time to perform flight measurements with the NASA CV 990 aircraft, thus the actual performance of this instrument has not been tested beyond what has been described above.

10. General Discussion of the ^{14}C Technique

The investigations described above show the evolution of a gas-phase radioisotope technique in the face of sometimes unexpected problems. Measurement of hydroxyl radicals, because of their relatively short chemical lifetime, rapid reaction with surfaces and low concentrations, may be more difficult than measurements of other species amenable to similar techniques, but the problems we faced are unlikely to be atypical. The problems of sampling cannot be overlooked. Methods for sampling transient species from an always turbulent atmosphere, at pressures much higher than usually employed in conventional flow systems, may bear little resemblance to those which have become accepted practice in the laboratory. Flow systems can make easier the detection of species present in very low concentration, but the very low conversions of our ^{14}CO tracer to $^{14}\text{CO}_2$ have shown that great care is required in avoiding spurious conversions by processes which are commonly regarded as quite insignificant, as well as the need for unusual precautions in the separation processes. In our case the sorption of traces of unreacted ^{14}CO by solid CO_2 , proved troublesome; in other systems one might anticipate problems with exchange reactions normally regarded as negligibly slow. Our experience suggests that, at impurity levels of 10^{-8} , surprises should be regarded as the norm, including batch-to-batch variations of impurities in reagents obtained from vendors.

We believe that gas-phase radioisotope methods have considerable potential in tropo-

spheric chemistry. Our measurements have shown that impurity levels of 10^{-9} can be obtained in relatively inexpensive, portable equipment intended for field use, together with correspondingly efficient separation of the product species. We have also shown that wall losses can be minimized by careful design. The measurements of hydroxyl concentration in surface air are already comparable in quality to ozone measurements as recently as 10 yr ago, and are improving rapidly. As experience is accumulated we will improve the quality of our data base on hydroxyl and examine extensions of the same techniques to other species.

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