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In situ observations

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In situ observations are defined as those made at the point where the instrument is located. Since a large variety of techniques have been used for *in situ* measurements, the general features, capabilities and problems of these techniques are reviewed. To illustrate capabilities and problems more specifically, examples of recent measurements are presented which have a bearing on the chlorofluoromethane–ozone problem. These include: (1) resonance fluorescence for the measurement of Cl and ClO, (2) grab and cryogenic collection of whole air samples for the measurement of $CFCl_3$ and CF_2Cl_2 (as well as CH_4, H_2, CO and N_2O), (3) impregnated filters for acid chloride, and (4) matrix isolation for HO_2 and NO_2.

Introduction

In situ measurements are those made at the location of the instrument. With this definition a large variety of techniques qualify as *in situ* measurements. Nevertheless, the fact that an instrument has to be carried to the site of the measurement and comes into contact with the sampled air, introduces several common limitations to all those techniques. Measurements can only be made along the flight track of the platform and are thus limited to horizontal or vertical profiles; global data coverage, which requires a large number of such profiles, would be difficult and costly to obtain from *in situ* observations. The fact that the measured air volume is usually inhaled into the instrument raises the possibility of sample modification either by contamination through outgassing or reaction with the surfaces of instrument and platform. Finally, since most *in situ* techniques are designed to measure specific trace constituents, they are usually less suited to exploratory search for unknown compounds.

On the other hand, there are certain advantages. Because they are designed to measure a specific constituent or small group of atmospheric constituents, *in situ* observations generally do not require much compromise and the most sensitive methods available can be employed; for practically any compound of interest an *in situ* technique can be developed. For the same reason, the precision of concentration measurements by *in situ* techniques is usually higher than that of remote measurements. At the same time, because a well defined and often small air volume is sampled, the sampling altitude is better defined, the height resolution in vertical profiles is greater, and the measured signal more easily interpreted than for remote sensing. Generally speaking, *in situ* measurements are better suited to the local instantaneous study of trace constituents, as is needed for detailed validation of chemical models, whereas remote sensing is better suited to providing global averages; in that sense, both approaches complement each other.

GENERAL OVERVIEW OF *IN SITU* TECHNIQUES

For a number of trace gases, the above mentioned problems of contamination or wall reaction were either small or could be overcome by proper design, and over the years a large number of successful *in situ* measurements have been reported. The most important ones are summarized in table 1. (Some older *in situ* measurements were reviewed by Ehhalt (1974).) *In situ* measurements can be grouped into two classes. In one group, the 'direct measurements', the measuring instrument is carried aloft, and the measurements are truly made *in situ*. In the second group, representative air samples are collected aloft for later analysis in the laboratory. Direct *in situ* techniques have the advantage that they can be adapted to the measurement of most trace constituents. Further, they offer the possibilities of real-time measurement and of taking many data points. However, the development of an instrument that has to function reliably on a balloon, aircraft or rocket requires substantial effort and time. The techniques relying on sample collection on the other hand, have the advantage that the sampling devices can be simple, rugged, and lightweight with small power requirements, i.e. very well suited for fieldwork. Furthermore, the analysis of the samples can be made under ideal conditions in the laboratory with already existing or slightly adapted equipment, which minimizes the cost of development. There are, however, disadvantages too. The air samples have to remain temporarily in a sample container, a requirement that increases the danger of sample modification due to contamination or wall reaction. Thus, collection techniques are limited to the measurements of trace constituents which are stable or can be stabilized. Besides the species measured and the measurement or sampling techniques employed, table 1 also gives an estimate of the precision of each method based on the errors quoted in the literature. Precision is here defined as the long term reproducibility of a measuring

TABLE 1. LIST OF TECHNIQUES USED FOR STRATOSPHERIC *IN SITU* MEASUREMENTS

('Direct measurement' refers to measurement at altitude; 'sample collection' involves collection at altitude and subsequent analysis in the laboratory.)

species measured	measurement or sampling technique	precision	investigator
Direct measurement			
HO, O, Cl, ClO HO_2, NO	resonance fluorescence	$\pm 50\%$	Anderson 1975, 1976, 1978; Anderson *et al.* 1977
NO	chemiluminescence	$\pm 20\%$	Ridley *et al.* 1975
O_3	chemiluminescence, electrochemical	$\pm 10\%$	
H_2O	frost point hygrometer	$\pm 10\%$	Mastenbrook 1974
$CFCl_3$, CF_2Cl_2† CCl_4, CH_3Cl†	e.c.-gas chromatography	$\pm 5\%$	Rasmussen 1977
H_2, CO	mercury oxide	$\pm 5\%$	Schmidt 1974; Seiler & Warneck 1972
Sample collection			
CH_4, H_2, CO	grab sampling	$\pm 5\%$	Ehhalt *et al.* 1974, 1975
$CFCl_3$, CF_2Cl_2, N_2O	grab sampling	$\pm 5\%$	Schmeltekopf *et al.* 1975, 1977
CH_4, CO, CO_2, H_2, N_2O	cryogenic sampling	$\pm 5\%$	Ehhalt *et al.* 1974, 1975
$CFCl_3$, CF_2Cl_2	cryogenic sampling	$\pm 10\%$	Heidt *et al.* 1975, 1976
HNO_3, Cl^-, F^-	impregnated filter	$\pm 30\%$	Lazrus *et al.* 1976
SO_2	impregnated filter	$\pm 30\%$	Jaeschke *et al.* 1976
HO_2, NO_2	matrix isolation	$\pm 30\%$	Mihelcic *et al.* 1978

† Measurements in lower stratosphere only.

method. Many experimenters seem to have underestimated precision and systematic errors of their data. Instrument precision has been improving steadily over the years, and not all the older measurements have the precision quoted here, whereas some of the most recent ones may have better precision than that stated (cf. W.M.O. 1977).

As indicated in table 1, the stratospheric distributions of many important trace constituents were obtained by direct *in situ* measurements: many of the available stratospheric O_3 data were obtained in this way owing to the fact that a lightweight cheap electrochemical O_3 sonde could be developed that allowed balloon measurements on a routine basis. Similarly, most of the stratospheric water vapour profiles were measured by a balloon-borne frost point hygrometer (Mastenbrook 1974). In this case, since the problem of contamination is severe and the experiment is much more difficult, correspondingly fewer H_2O profiles are available. Also in the case of NO, much of the vertical distribution was measured by a direct *in situ* technique based on a chemiluminescent instrument (Ridley *et al.* 1975). The most exciting direct measurements, however, are the experiments of Anderson (1975, 1976) and Anderson *et al.* (1977), who measured stratospheric concentrations of free radicals, using a resonance fluorescence technique. This experiment will be discussed below.

Of the collection techniques grab sampling is the simplest. A previously evacuated container is opened at the sampling site, allowed to fill to ambient pressure, and closed again. The samples are then returned to the laboratory for analysis. Because of its simplicity this technique has been used widely. However, at high altitudes air sample pressure becomes low and the ratio of surface area to sample amount unfavourable. Accordingly preservation of sample integrity becomes more difficult, and the application of grab sampling has been limited to the less reactive and more abundant species, such as CH_4, CO, CO_2, H_2, N_2O, CF_2Cl_2 and $CFCl_3$, and to the lower part of the stratosphere. To overcome the problems of small sample size and to extend measurements to higher altitudes, various methods of sample compression have been tried. The cleanest and most widely applicable of these techniques is cryogenic sampling, which collects large samples by condensing ambient air in sample cylinders cooled by liquid Ne, He, or H_2. Still, even the cryogenic collection of whole air samples is limited to the more stable gases. For certain reactive trace gases, selective sampling techniques have been developed that collect a specific trace constituent or group of trace constituents but discard the bulk of the air In this way, enrichment factors of many orders of magnitude can be achieved, and the method can be quite sensitive. The most widely applied selective sampling technique is the impregnated filter method, which has been used by Lazrus & Gandrud (1974), Lazrus *et al.* (1975, 1976), and Mroz *et al.* (1977) to measure acidic gases involving gaseous nitrate, chloride and fluoride. Another technique of this kind is the matrix isolation technique, which even allows the measurement of free radicals.

Although table 1 is by no means complete, it indicates that a large body of information has been gathered by *in situ* techniques. To illustrate *in situ* techniques, their capabilities and their problems in more detail, examples of different methods and their results are described below. Following the lines of a previous review (Ehhalt 1978), the discussion is essentially limited to measurements of chlorine and fluorine compounds presenting the most recent data. Only in the case of our own measurements are other compounds included.

Direct measurements

Radical measurement by resonance fluorescence

Probably the most advanced *in situ* measurements are the resonance fluorescence experiments for measuring the radical concentrations of O, OH, HO_2, NO, Cl and ClO (Anderson 1975, 1976, 1978; Anderson *et al.* 1977). We will limit our discussion to Cl and ClO, although the instrument used is the same in principle for all these radicals. It is essentially a flow tube suspended on a parachute and dropped from a balloon at altitudes around 45 km. During the fall, ambient air enters from below and flows through the tube at high speeds, between 100 m/s at high altitudes to 30 m/s at low altitudes. This minimizes wall reactions. In order to detect Cl or ClO radicals, a beam of photons at 118.9 nm wavelength from a Cl lamp with a filter of gaseous O_2 is passed perpendicularly through the air stream. The resonant scattered photons are monitored by a detection system mounted at right angles to flow and light beam. The background signal resulting from photons reflected from the walls, photons Rayleigh-scattered by the air molecules and some solar photons reaching the scattering volume, is recorded in flight by eliminating the observed species by a suitable reaction. In the case of ClO which does not fluoresce, the measurement of the background signal does not require a reaction. However, to measure ClO, it is converted to Cl via the reaction $ClO + NO \rightarrow Cl + NO_2$, and the resulting additional Cl atoms are detected by resonance fluorescence. The reactant gas is injected in short alternating intervals through a diffuser loop at the air inlet. Absolute calibration, required to account for geometry and efficiency factors, is performed in the laboratory before and after a stratospheric flight by flowing known amounts of the observed radical through the system. The measured Cl volume mixing ratio are shown in figure 1 and the measured ClO volume mixing ratios are shown in figure 2 (Anderson *et al.* 1977, Anderson 1978). They reflect the newest values given by

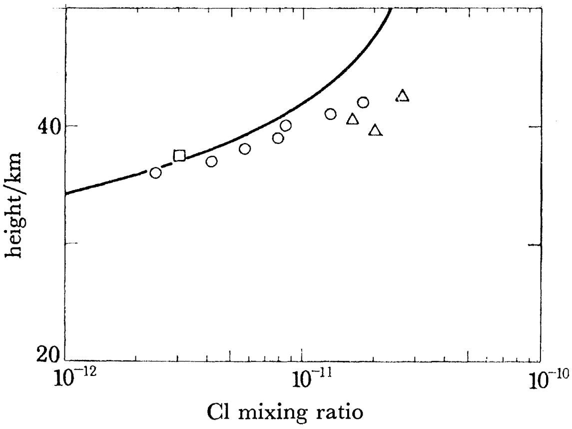

FIGURE 1. Stratospheric measurements of the Cl volume mixing ratio over Palestine, Texas, 32° N (Anderson *et al.* 1977). The curve is a theoretical profile calculated for 30° N latitude and equinox conditions. ○, 28 July 1976; △, 2 October 1976; □, 8 December 1976; ——, K. F. A. model.

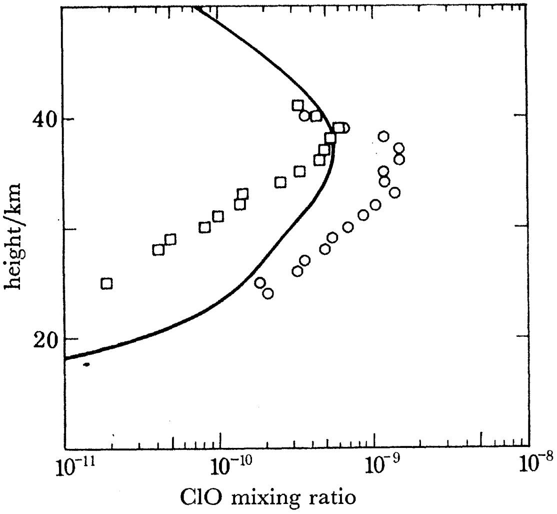

FIGURE 2. Stratospheric profiles of the ClO volume mixing ratio measured over Palestine, Texas, 32° N (Anderson *et al.* 1977; Anderson 1978. The full curve is a theoretical profile calculated for 30° N latitude and equinox conditions. ○, 28 July 1976; □, 8 December 1976; ——, K.F.A. model.

Anderson for these flights (Anderson 1978). The measurements were made over Palestine, Texas, 32° N. During 1977 Anderson *et al.* have measured four more ClO profiles which have been discussed at various conferences. Like the ones shown here, they all reveal a strong increase in the lower and middle stratosphere, sometimes reaching a maximum between 35 km and 40 km altitude. Although the data from individual profiles are internally quite consistent, Anderson *et al.* observed large variations between the various profiles, up to one order of magnitude between the maximum and minimum values at a given altitude. There is an indication of a seasonal variation with higher values in July. However, these high values, especially a profile from July 1977 which reached a maximum mixing ratio of $8/10^9$ at 40 km altitude are difficult to reconcile with a number of other observations as well as presently held views on the stratospheric Cl budget. If ClO concentrations were indeed as large as the July 1977 profile seems to indicate, the present understanding of stratospheric O_3 chemistry would demand O_3 concentrations a factor 2–3 lower than the average O_3 profile. However, the O_3 concentrations measured along with that flight showed a reduction of only about 20% (Anderson 1978), which means that such high ClO concentration could have persisted only for a short time and only locally. Furthermore, the present consensus of sources of stratospheric Cl, mainly from CH_3Cl, CCl_4, $CFCl_3$, CF_2Cl_2, limits the sum of all chlorine compounds to $2.3/10^9$, a number in good theoretical agreement with the HCl measurements quoted below. These $2.3/10^9$ for total chlorine are however much less than the maximum mixing ratio of $8/10^9$ measured for ClO alone during the flight in July 1977. In fact, already the ClO profile from July 1976, shown in figure 2 to reach about $1.6/10^9$, would appear fairly high. The four other ClO profiles obtained by resonance fluorescence show reasonable agreement with the mixing ratios predicted from a one dimensional model which are also indicated in figure 2.

There are further, remote measurements of stratospheric ClO, unfortunately also with conflicting results. Measurements from an aircraft-borne microwave spectrometer to detect emission of infrared radiation in the millimetre wavelength range from stratospheric ClO indicated significant amounts of ClO (Waters *et al.* 1978). Comparison of the theoretically calculated lineshapes to the observed ones suggest ClO to be present with peak mixing ratios between $0.5/10^9$ and $1/10^9$. Although these measurements, which were made in June and August 1977, probably still have large errors, they clearly indicate much lower ClO abundances during the summer than those obtained by the resonance fluorescence technique. In addition, there are preliminary data from Menzies previewed in Upper Atmospheric Programs Bulletin (October 1978). Using a balloon-borne laser heterodyne radiometer the following mixing ratios were measured on 20 September 1978, over Palestine, Texas: $(2.5 \pm 0.6)/10^9$ at 37.5 km altitude, $(1.7 \pm 0.4)10^9$ at 33.8 km, $(0.8 \pm 0.2)/10^9$ at 32.8 km, and $(0.22 \pm 0.06)/10^9$ at 29 km. Since the data were taken at sunset (solar zenith angles between 90° and 95°) and ClO has a fairly strong diurnal variation at these altitudes, the corresponding daytime concentrations should be higher by about a factor 2. This would bring the value at 37.5 km into fair agreement with the high values from the July 1977 profile by Anderson (1978). The gradient of the profile by Menzies appears much steeper than Anderson's measurements. This could, however, be due to the fact that the measurements were made in sequence during the rapid setting of the Sun. An explanation will have to await the full publication of these data. Because of the still conflicting measurements it remains difficult to accept the present experimental data as corroboration of the calculated ClO profile as long as the discrepancies are not explained or removed by further measurements.

The Cl measurements shown in figure 1 do not show a particular excess of Cl atoms. For those flights, the Cl/ClO ratio is also in reasonable agreement with the theoretical prediction.

Collection techniques

Grab sampling

The oldest and simplest collection technique is grab sampling. Because the size of the collected air samples becomes small, about 10 cm^3 s.t.p., at 40 km altitude, stratospheric grab sampling places particularly high requirements on the cleanliness of the collection system. These requirements become even more stringent when halocarbons with mixing ratios as low as 10^{-12} are to be measured, and extreme care has to be taken in the choice of components and materials, cleaning and sampling procedures, and the vacuum integrity of the sample containers. A rather sophisticated balloon-borne grab sampler has been developed by the Aeronomy Laboratory of N.O.A.A., in Boulder (Schmeltekopf *et al.* 1976), whose results will be used to illustrate the capabilities of this method. The original sampler consisted of five evacuated 7.5 l stainless steel spheres with specially designed valves. Currently, samplers with up to twelve sample containers are in use. The sphere halves are electropolished inside before welding, passivated after welding by exposing the interior surface to hexamethyldisilazane and vacuum baked at 200 °C. This passivation proved necessary because adsorption sites created at the inner surface during the welding of the spheres chemisorb halocarbons, including $CFCl_3$, from the sample. In fact, some of the early measurements seem to have suffered from a loss of $CFCl_3$, whereas contamination generally turned out to be less of a problem than was anticipated. The present bigger payloads have lost some of their original advantage of being particularly lightweight and compact. Still, they are small enough to be hand launched by a small crew on relatively small balloons. After reaching altitude the payload is cut from the balloon and dropped on a parachute. The samples are collected during rapid descent, which causes any contamination emanating from the package to be flushed away from the inlets. After recovery, the samples are returned to the laboratory and analysed among others for $CFCl_3$, and CF_2Cl_2 by a gas chromatograph equipped with an electron capture detector. Despite the low concentrations encountered, detector sensitivity never presented a serious problem since the electron capture detector is extremely sensitive for halocarbons. However, it took a while before adequate calibration procedures were devised and intercalibration among the various laboratories making such halocarbon measurements became satisfactory. The most recent intercalibrations show that agreement between the laboratories that provided most of the stratospheric $CFCl_3$ and CF_2Cl_2 data is rather good, better than 5 %.

The data obtained at different latitudes by this highly mobile system are shown below in figure 3 and 4, together with the data from cryogenic sampling discussed below.

Cryogenic sampling

Cryogenic sampling is a method for collecting large-volume air samples in the stratosphere that offers the advantages of simultaneous measurement of a number of trace gases and considerable reduction of wall reaction and contamination from the inner surfaces of the sample containers. For example, a 7.5 l grab sample collected at 30 km altitude yields 90 cm^3 s.t.p. of air; a cryogenic sample yields 10 l s.t.p. in one tenth of the volume. Thus the sample amount to surface ratio is improved by a factor of more than 100; the influences of contamination and wall reaction are reduced accordingly. As an example we will discuss the balloon-borne cryogenic sampler developed at the National Center for Atmospheric Research (N.C.A.R.) in Boulder (Ehhalt *et al.* 1974; Lueb *et al.* 1975), which was in a slightly modified version also used by Fabian *et al.* (1978). The cryogenic sampler consists of an array of 8 or 16 electropolished stainless steel cylinders immersed in a dewar filled with liquid neon. Cleaning procedures, vacuum bake-out and passivation are similar to those described for grab sampling. Each cylinder is connected to a common inlet manifold by a bellows-sealed stainless steel high vacuum which is driven by a motor. At liquid neon temperature, about 30 K, most gases in the air are frozen solid with vapour pressures below 10^{-4} Torr. Hydrogen, helium and neon are not condensed and remain gaseous. To prevent fractionation, the sampling cylinders are designed in such a way that the inflowing air effectively prevents the back diffusion of the uncondensable gases (Lueb *et al.* 1975). Thus each tube acts as an efficient cryopump. The samples are also collected during descent. However, sampling times are longer, up to 20 min at maximum altitude and the payload has to descend slowly (at a rate of 50 m/min) while it is suspended on the balloon. To prevent contamination from the balloon, the payload is located 150 m below. To minimize contamination from the payload itself, the inlet line is extended 6 m below the payload and flushed several times before each sampling by a separate cryopump. After being warmed up and returned to the laboratory the samples are analysed for CO_2, CO, CH_4, H_2 H_2O, N_2O, $CFCl_3$, and CF_2Cl_2, mostly by gas chromatography (Ehhalt *et al.* 1974, 1975; Heidt *et al.* 1975; Fabian *et al.* 1978).

The most recent data from both of the above discussed sampling techniques for CF_2Cl_2 and $CFCl_3$ are shown in figures 3 and 4. They include, largely owing to the efforts of the N.O.A.A. group, vertical profiles in tropical and arctic latitudes (Schmeltekopf 1978; Goldan 1978, private communication). To allow identification of an eventual variation with latitude these measurements are shown separately. The tropical data were taken over Panama 8° N and Northern Brazil 8° S. Because of their scarcity, the data in high latitudes include antarctic measurements as well. The profiles were collected in spring or summer. The largest number of profiles is available for mid-northern latitudes from various authors (Schmeltekopf *et al.* 1976; Heidt *et al.* 1976; Fabian *et al.* 1978). These laboratories have intercalibrated their standards and found good agreement. The measurement errors should be less than 5 %. Regardless of latitude, CF_2Cl_2 shows a steep drop with altitude in the stratosphere starting from a value of about 240 parts/10^{12} at the tropopause. It appears, however, that the steepness of the gradient does depend on latitude. At middle and high latitudes the gradients are 20 parts/10^{12} per kilometre in the lower stratosphere, whereas the equatorial gradient amounts to only 7 parts/10^{12} per kilometre. Accordingly the average mixing ratio at 25 km altitude has dropped to 43 parts/10^{12}, nearly a factor of 6, in high latitudes whereas the corresponding value in tropical latitudes is 175 parts/10^{12}, only a factor 1.4 lower.

It appears that the isopleths of constant CF_2Cl_2 mixing ratio in the stratosphere are more steeply inclined with latitude than the contour of the tropopause. This is a surprising finding since, because of the higher photon fluxes in the tropics, one would expect a faster photolysis of CF_2Cl_2 and thus a steeper decrease of the concentration with altitude. The slower decrease measured points to a much faster vertical transport in the equatorial zone at least during the time of sampling. Looking at the scatter of the data at mid-latitudes it becomes clear that a conclusion of this kind is still preliminary. Above 25 km the scatter increases and reaches nearly a factor of 10 between the extreme values at an altitude. Since for the present data the measurement errors are much smaller than that, the fluctuations must be natural, presumably due to large scale transport processes in a concentration field with strong vertical and somewhat weaker horizontal gradients. Like the temperature profiles concentration profiles of longer lived trace gases like CF_2Cl_2 are influenced by advection of air masses of different origin and thus depend on the momentary wind field. To derive a reliable average of the meridional concentration field more profiles have to be measured, particularly at tropical latitudes.

Figure 3 shows also a theoretical profile of CF_2Cl_2 calculated for equinox conditions and 30° N latitude. It falls consistently above the measurements. Some of the discrepancy could be explained by the fact that most mid-latitude data were collected between 40° and 55° N

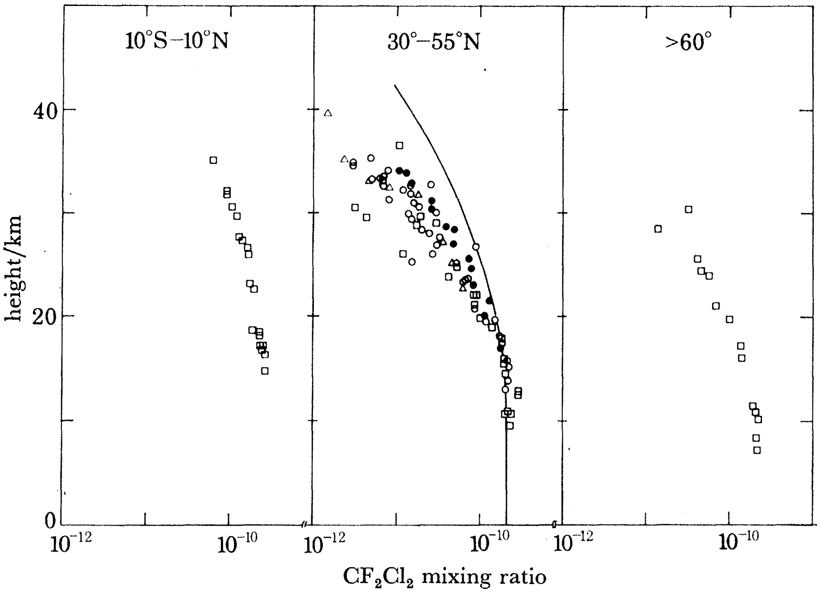

FIGURE 3. Vertical profiles of the CF_2Cl_2 volume mixing ratio at different latitudes. The data for high latitudes include measurements over Antarctica. The theoretical curve shown for mid-latitudes was calculated for 30° N and equinox conditions. △, Yorkton; ●, Heidt *et al.*; □, Schmeltekopf *et al.*; ○, Fabian *et al.*; ——, K.F.A. model.

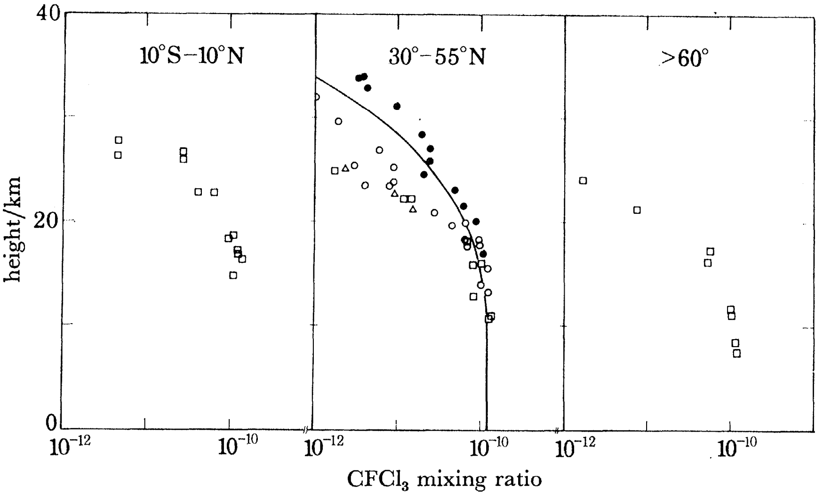

FIGURE 4. Vertical profiles of the $CFCl_3$ volume mixing ratio at different latitudes. The data for high latitudes include measurements over Antarctica. The theoretical curve shown for mid-latitudes was calculated for 30° N and equinox conditions. △, Yorkton; ●, Heidt *et al.*; □, Schmeltekopf *et al.*; ○, Fabian *et al.*; ——, K.F.A. model.

where the latitudinal dependence indicates a steeper gradient. But even the data from 30° N, indicated by the full dots, still fall below the theoretical curve. Most probably this is due to inadequate treatment of the transport in the one dimensional model.

The corresponding $CFCl_3$ data show a much faster fall-off in the stratosphere (figure 4). This is to be expected from its higher photolysis rates. The latitudinal variation of the vertical gradient is less obvious but still present, at least in the lower stratosphere. For $CFCl_3$ the mid-latitude model calculation agrees with the measurements. The photolysis becomes so fast above 30 km that inaccuracies in transport at or above that altitude scarcely influence the calculated profiles.

The samples collected by cryogenic sampling are so large that aliquots can be used for the measurement of other compounds. These include CH_4, H_2, N_2O and CO, CO_2 and H_2O. Results from our own work over Southern France are reviewed briefly in the following. It was done in collaboration with the Max-Planck-Institutes in Lindau and Mainz (cf. Fabian *et al.* 1978). The general flight data are summarized in table 2. The measurements quoted below are from the Institute of Atmospheric Chemistry, K.F.A. Jülich (Ehhalt *et al.* 1977*b*; Fabian *et al.* 1978).

TABLE 2: FLIGHT DATA OF PROFILE MEASUREMENTS IN 1977 OVER SOUTHERN FRANCE, 44° N LATITUDE

flight no.	7701/I	7702/II	7704/I	7705/I
date	7 June	16 June	12 Sept	26 Sept.
maximum altitude/km	35.3	34.8	33.5	32.8
tropopause altitude/km	*ca.* 12.1	*ca.* 12.2	*ca.* 13.2	*ca.* 12.1
number of samples	8 stratosphere 8 troposphere	5 stratosphere	8 stratosphere 16 troposphere	8 stratosphere
date of analysis (K.F.A.)	9–14 June	17–21 June	15–16 Sept.	30 Sept.–2 Oct.

CH_4 AND CO: The CH_4 and CO content of the air samples were measured simultaneously by using a 1 m column of 5 A molecular sieve and a flame ionization detector; CO was converted to CH_4 over a Ni catalyst at 400 °C before detection. The resulting CH_4 profiles are plotted in figure 5. The use of the true altitude in figure 5 introduces some extra scatter in the data of the flights. On the whole, however, the various profiles show a rather good agreement, decreasing steadily from $1.64/10^6$ by volume at the tropopause to $0.6/10^6$ by volume at 34 km altitude. The agreement between flights is much closer than had been observed previously over N.C.A.R's balloon station in Palestine Texas, 32° N, where profiles occasionally showed rather distinct layers (Ehhalt *et al.* 1974). There are two reasons for this finding. The first is that the profiles over Southern France were all obtained during situations of weak stratospheric winds in late spring or late summer, when the probability of long range horizontal advection of air masses with different CH_4 concentrations is relatively small. Secondly, N.C.A.R.'s balloon flights at 32° N were occasionally within the downward branch of the Hadley circulation, which introduces a steepened gradient just above the tropopause. Apart from the latter effect the agreement between the present profiles and N.C.A.R.'s measurements is rather good, in particular both data sets observe about $0.6/10^6$ by volume around 35 km altitude. Figure 5 also shows a CH_4 profile over Southern France obtained by infrared spectroscopy (Ackerman *et al.* 1977). The data points shown here are the average from several lines. Although the agreement between the *in situ* measurements and this profile is much better than with the older infrared measurements (cf. Ackerman *et al.* 1977), the infrared profile still indicates a somewhat steeper gradient than those obtained by us. The tropospheric measurements lie uniformly close to 1.64/10⁶ by volume. This agrees also well with N.C.A.R.'s most recent tropospheric profiles over Eastern Texas (Heidt *et al.* 1976). These concentrations, however, are higher than N.C.A.R.'s earlier measurements from 1965–1967 over Scotts Bluff, Nebraska and the Eastern Pacific which averaged 1.41/10⁶ by volume (Ehhalt & Heidt 1973). Since N.C.A.R. has a continuous sequence of intercalibrated working standards this increase should be real (L. Heidt, private communication).

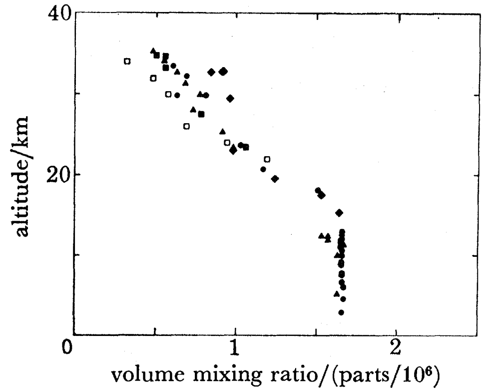

FIGURE 5. Vertical profiles of CH_4. The relative accuracy of analysis was ± 2 %. The open squares represent the results from a balloon-borne infrared experiment (Ackerman *et al.* 1977. ▲, 7 June 1977; ■, 16 June 1977; ●, 12 September 1977; ◆, 26 September 1977.

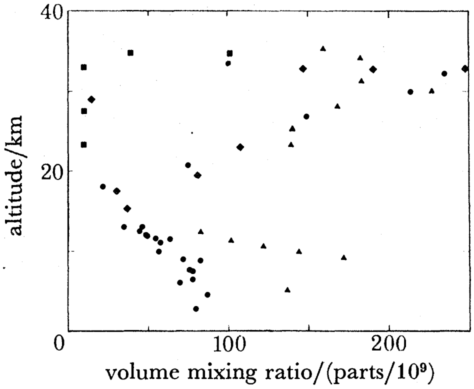

FIGURE 6. Vertical profiles of CO. The results above 20 km altitude are influenced by contamination. The relative accuracy of analysis was ± 3 % or ± 5/10⁹ by volume. ▲, 7 June 1977; ■, 16 June 1977; ●, 12 September 1977; ◆, 26 September 1977.

The corresponding CO measurements are shown in figure 6. The increase of the CO concentration shown above 20 km altitude and the large scatter of the data at these altitudes are most likely due to contamination. Unfortunately, at the time of writing the laboratory tests to identify the cause of this contamination are not conclusive. The speculation is that organic exhaust vapours from the launch vehicle, which find their way into the inlet line react when exposed to ozone-rich air during sample collection at altitude to form CO. It appears that by the time the balloon reaches 20 km altitude the inlet line is flushed free from contamination and data below that altitude should be correct. The tropospheric data showing a decrease with altitude fall well within the range previously observed.

H_2 : H_2 was measured by using a 3 m column of 5 A molecular sieve and a He ionization detector. The H_2 profile obtained is shown in figure 7. The individual profiles show a very similar behaviour and the scatter of the data points is small. Nearly all of it could be explained by the relative accuracy of the analysis, which is about 5 %. The stratospheric part shows a weak, linear decrease in the mixing ratio from 0.55/10⁶ by volume at the tropopause to about 0.45/10⁶ by volume at 35 km altitude. There is no hint of a slight maximum of about 0.6/10⁶ by volume at 28 km altitude which was occasionally indicated in some of the N.C.A.R. flights over Palestine, Texas. The troposphere does not show any vertical gradient at all. The average of 0.55/10⁶ by volume differs somewhat from the value of 0.5/10⁶ by volume obtained during aircraft flights in 1966, 1967, 1971 and 1972 due to a difference in absolute calibration (Ehhalt *et al.* 1977*a*).

N_2O: N_2O was measured together with $CFCl_3$ and CF_2Cl_2 on a gas-chromatograph equipped with a 3 m Porasil C column and an electron capture detector. To ensure better resolution of N_2O and a faster elution of the heavier halocarbons the column was temperature-programmed, starting at −10 °C and rising to 150 °C in 8 min. The N_2O data are shown in figure 8. Similarly to CH_4, the N_2O measurements from the four flights showed quite consistent results.

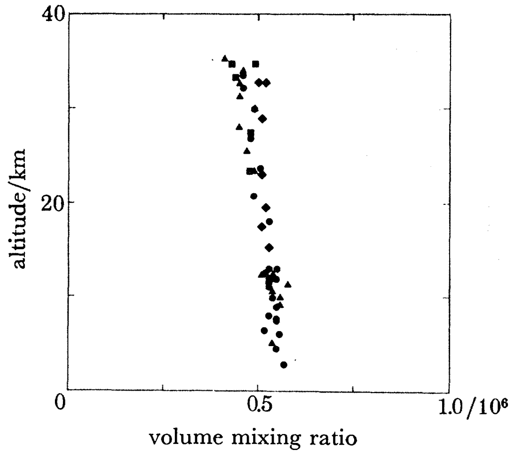

FIGURE 7. Vertical profiles of H_2. The relative accuracy of analysis was ±5%. ▲, 7 June 1977; ■, 16 June 1977; ●, 12 September 1977; ◆, 26 September 1977.

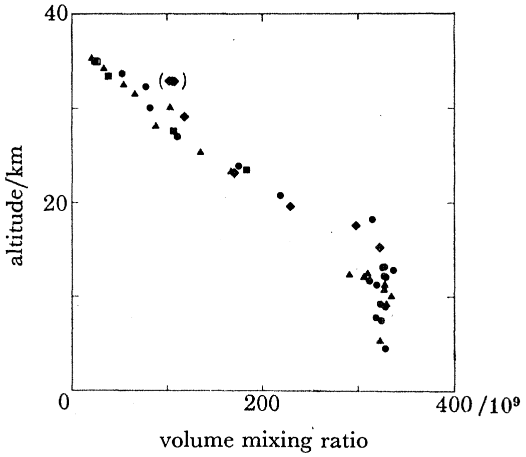

FIGURE 8. Vertical profiles of N_2O. The relative accuracy of analysis was ±5% or $\pm 3/10^9$ by volume. ( ): Collected during floating period. ▲, 7 June 1977; ■, 16 June 1977; ●, 12 September 1977; ◆, 26 September 1977.

Aside from the uppermost data from 26 September 1977, which were collected during float, the observed average fluctuations above 20 km are less than 5%, presumably for the same reasons as discussed for CH_4. The resulting average profile shows a strong, nearly linear decrease from $330/10^9$ by volume at the tropopause to about $20/10^9$ by volume at 35 km, although in flight 7704 nearly tropospheric N_2O mixing ratios persist to 18 km altitude, well above the tropopause. The profile agrees well with the stratospheric N_2O data of Schmeltekopf *et al.* (1977) over Wyoming, 41° N. The troposphere shows a rather uniform N_2O concentration with values between 325 and $335/10^9$ by volume and an average of $327/10^9$ by volume in good agreement with the tropospheric averages reported by Rasmussen (1977) and Goldan (1977).

SELECTIVE SAMPLING

Impregnated filter method

An interesting selective sampling technique used in the stratosphere is the measurement of acidic gases by means of a base-impregnated filter. The technique was developed by Lazrus *et al.* (1975), using an IPC-1478 aerosol filter. Before collection of gaseous acidic chloride, essentially the sum of HCl, $ClONO_2$, and if present HOCL, the filters are washed and purified to minimize the chloride background; they are then impregnated with tetrabutylammonium hydroxide, a strong organic base, which mixes with the organic oil already present on the filter and remains 'sticky' even at the low stratospheric sampling temperatures. To obtain the blank values, the filters are subdivided into four sections. Two of the sections are impregnated, and two remain untreated. One impregnated section and one unimpregnated section are shielded from the airstream by a mask, so that they do not collect and remain as a blank. The filters were flown on aircraft as well as on balloons. In the first case the ram pressure provides the airflow; on the balloons, airflow is maintained by a blower. In either case the airflow is monitored. Collection efficiency for HCl is reported to be now 100 %; for $ClONO_2$ to be at least 80 % (Lazrus *et al.* 1977). The possible collection of HOCl has not been considered by the authors. Measurement of the collection efficiency of ClO is in progress. The effect of CH_3Cl and other halocarbons should be small. In the laboratory the filter sections are separated and washed. The extracted solutions are analysed for the chloride ion by a colorimetric method. The concentrations of the gaseous compounds are obtained after subtracting the contributions from particulate matter and the blank, which are determined from the unimpregnated and masked sections, respectively. An error of ± 30 % was quoted for the acidic chloride measurement by Gutowsky (1976, p. 309). Figure 9 shows the annual average data for acidic chloride, which were obtained over Holloman Air Force Base, New Mexico 33° N. It also contains some of the more recent HCl data obtained by remote infrared techniques. Lazrus *et al.* did not find a seasonal variation but they found rather regularly a minimum in the acidic chloride at around 30 km altitude which interrupts a general increase with altitude in the stratosphere. There is no evidence for such a minimum in the infrared data for HCl. On the contrary some indicate an intermediate maximum at about the same altitude which causes a relatively large discrepancy between the *in situ* and remote measurements at the heights around 30 km. Otherwise the agreement is reasonable. If for the moment we accept the *in situ* measurements of acidic chloride as reliable,

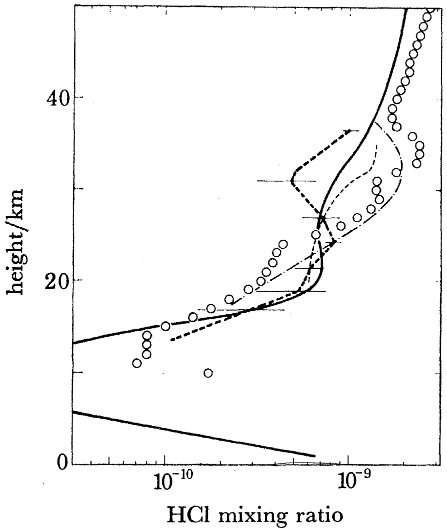

FIGURE 9. Average stratospheric volume mixing ratio profile of gaseous acidic chloride over Holloman Air Force Base, N.M. 33° N (curve labelled Lazrus *et al.*). The other data represent individual profiles of the HCl volume mixing ratio measured by infrared spectrometry. The full curve represents a theoretical profile calculated for 30° N latitude and equinox conditions. - - -, Lazrus *et al.* 1977; ○, Evans, 1 December 1977; – – –, Raper *et al.* 1977; –·–·–, Eyre & Roscoe 1977; ——, K.F.A. model.

their agreement with the optical HCl data and even more their tendency to be smaller around 30 km altitude and would indicate that the other acidic chloride gases, $ClONO_2$ and HOCl have very low concentrations, certainly lower than presently predicted by models. This is somewhat difficult to accept because the calculated HCl profile agrees reasonably well with the ones measured by the infrared techniques and the total chlorine, essentially the sum of HCl, $ClONO_2$ and HOCl mixing ratio, has to be at least $2/10^9$ to which HCl contributes only $1/10^9$.

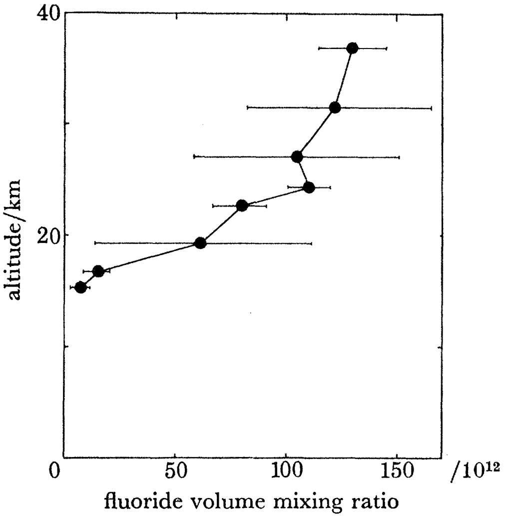

FIGURE 10. Vertical profile of stratospheric gaseous acidic fluoride (Mroz *et al.* 1977).

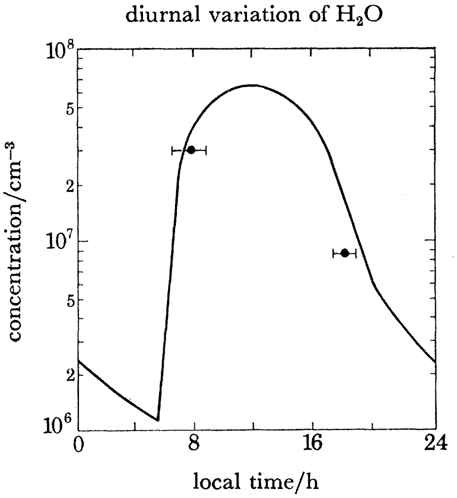

FIGURE 11. Comparison of the experimental HO_2 concentrations (Mihelcic *et al.* 1978) with a theoretical diurnal variation calculated for 30 km altitude, 30° N latitude and equinox conditions (Logan *et al.* 1978).

Similar measurements were made for the total stratospheric acidic fluoride concentrations (Mroz *et al.* 1977). Besides HF, gaseous acidic fluoride includes COF_2, another degradation product of chlorofluoromethanes. The data are summarized in figure 10. They agree reasonably well with a determination of the HF/HCl ratio of 0.1 in the height range from 14 to 30 km by Farmer & Raper (1977) and the HCl mixing ratios in figure 9.

Matrix isolation

There are several ways in which cryogenic techniques can be used to selectively sample trace substances and to reject the bulk of the air sample. One of the most interesting is the so-called matrix isolation, a well known laboratory technique. In its application to stratospheric measurements, this technique employs the condensation of a solid, inert matrix of CO_2 on a cold surface for sample collection (Mihelcic *et al.* 1978). In the process of matrix deposition, free radicals and other condensable trace gases are trapped and embedded in the matrix structure. As long as there is a large surplus of matrix molecules and the matrix is kept sufficiently cold, the free radicals remain isolated and cannot react with each other. The use of atmospheric CO_2 for matrix deposition offers two critical advantages. First, large enrichment factors can be obtained. Second, liquid nitrogen temperature, 77 K, is sufficient for sample collection. This greatly reduces logistic problems in the field and allows one to build a rugged, lightweight sampler suitable for balloon-borne measurements. The sampler consists essentially of a liquid nitrogen cooled cold finger on which the CO_2 matrix is deposited, a liquid nitrogen cooled cryopump which absorbs the non-condensable gases, essentially N_2 and O_2, and maintains the airflow, and a nozzle which allows the air to enter the sampling device in a narrow, well defined beam enveloping the cold finger. The nozzle can be opened and closed by a valve. After sample collection and recovery of the payload, the cold sample is returned to the laboratory and its radical content is analysed by electron paramagnetic resonance (e.p.r.) Matrix isolation combined with e.p.r. detection can be applied to detect nearly all radicals. However, a CO_2 matrix at 77 K is not yet completely rigid and light radicals such as OH can still diffuse through the lattice. Thus the method is currently limited to measuring HO_2 and NO_2. The spectra of these two major radicals are sufficiently different to allow unscrambling of the composite spectrum one expects from stratospheric samples (cf. Mihelcic *et al.* 1978). Two measurements of stratospheric HO_2 by this method have been reported so far. One was made over North Germany, 52° N, on a sample collected at 32 km altitude between 6.40 and 9.00 a.m. on 8 August. It gave a concentration of 3×10^7 cm^{-3}. The other was obtained from a balloon flight over Holloman Air Force Base, New Mexico, 33° N, on 4 March 1977, 4.45–5.48 p.m. at 29.8 km altitude. The HO_2 concentration was 8.5×10^6 cm^{-3}. Because of difficulties in the laboratory calibration, both measurements have an error of about a factor of 3. The data are compared to a theoretical curve of the diurnal HO_2 variation (Logan *et al.* 1978) in figure 11. The curve was calculated for 30° N. and equinox conditions. To match the experimental points to the proper solar zenith angle, they were plotted at a slightly shifted daytime. Despite the different sampling locations the agreement between theoretical prediction and measured points is surprisingly good. In principle it should also be possible to measure ClO with this technique. However, so far no measurements have been reported.

CONCLUSION

Although limited to a few examples, the foregoing discussion shows that *in situ* techniques have provided numerous interesting measurements. In particular, they provide the best and, in some cases, the only way to measure rare and reactive species such as radicals. Such measurements will present a much more stringent test of our understanding of stratospheric chemistry than was previously possible.

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