ENVIRONMENTAL POLLUTION MONITORING AND RESEARCH PROGRAMME

No. 39

REPORT OF THE THIRD WMO EXPERT MEETING ON ATMOSPHERIC CARBON DIOXIDE MEASUREMENT TECHNIQUES
(Lake Arrowhead, CA, USA, 4-8 November 1985)

October 1986

A Contribution to the Global Environmental Monitoring System (GEMS)
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1. OPENING OF THE MEETING

On behalf of the Secretary-General of the WMO, Prof. G.O.P. Obasi, Mr. A. Köhler welcomed the participants and thanked them and their affiliated administrations for supporting their attendance. He also thanked Professor Charles D. Keeling for his assistance in preparing the meeting and for providing excellent meeting facilities on the premises of the Lake Arrowhead Conference Centre of the University of California. He underlined the excellent collaboration of international experts who for many years have contributed to this important monitoring activity. He noted with satisfaction that practically all laboratories which have been carrying out CO₂ measurements or are involved in preparing calibration standards were able to attend, a positive demonstration of co-operation in the field of environmental monitoring and research. It was much regretted, however, that scientists from Japan, Sweden and the USSR could not participate. However, the attendance of scientists from countries preparing themselves to carry out atmospheric carbon dioxide observations was regarded as very helpful towards a continued globally standardized CO₂ observation system. A list of participants is reproduced in Annex III.

2. ADOPTION OF THE AGENDA AND ELECTION OF OFFICERS

The tentative agenda distributed in advance of the meeting was slightly modified. The organization of this report corresponds to the agenda as adopted. The group elected Dr. W.P. Elliott (ARL/NOAA, USA) and Dr. G.I. Pearman (CSIRO, Australia) as the two chairmen sharing the work equally and Dr. J.T. Peterson (GMCC, NOAA) as the Rapporteur.

3. SCIENTIFIC REQUIREMENTS

3.1 The current situation regarding accuracy and precision

Long term changes of atmospheric CO₂ are now about 1 to 2 ppmv/year and are likely to continue in this range for some time. To monitor these changes would require only one or two stations and a system precision of 0.5 to 1.0 ppm. However, the detection of variations of this growth rate, the detection of changes in the amplitudes of the annual concentration cycle and the determination of latitudinal gradients, place more stringent requirements on the network, its instrumentation and standard reference gases. These requirements include inter-laboratory imprecision of lower than 0.1 ppmv for analysis of regional scale spatial gradients. A thorough discussion was presented at the 1981 WMO/UNEP/ICSU Meeting on Instruments, Standardization and Measurement Techniques for Atmospheric CO₂ (Environmental Pollution Monitoring and Research Programme series report No. 5, table 2.3).

It is important to measure these effects to validate predictions of numerical models. It is large models of the carbon cycle that will be used to anticipate the atmospheric concentration in the next century for given fossil-fuel emissions of CO₂. More important, if we gain confidence in these models, they could be used to devise fossil-fuel policy options to prevent air concentration from exceeding a specified amount.
Experience of the past few years has underscored the need for improved precision. The El Niño of 1982–83 was associated with changes in CO₂ concentrations and its recent growth rate. Indeed analyses suggest that throughout the modern atmospheric CO₂ record, interannual variations have occurred with a 2–3 year period. Analyses of CO₂ changes during this event have already shown the importance of measurements precise to 0.1 or 0.2 ppmv. Suggestions that the annual amplitudes are changing and that there are differences in this quantity among the stations, stress the need for improved precision. The group anticipated the need for precisions to be better than 0.1 ppmv. This implies that laboratory secondary standards should be assigned values to a precision of a few hundredth of a ppmv.

These scientific requirements for measurement accuracy and precision can be met currently as follows. The infrared instrumentation presently in use in the WMO network is capable of determining a mean concentration precise to about 0.1 ppmv with repeated measurements on the same gas mixture. If the measurements are made several days apart deviations not greater than 0.2 ppmv are achievable. By repeating these measurements it is possible to determine a mean concentration to about 0.1 ppmv. It appears possible that improvements can also be made in non-dispersive infrared (NDIR) instrumentation which could improve its precision as well.

Interstation imprecision is not necessarily as low as 0.1 ppmv. With the almost universal introduction of CO₂-in-air reference standards the situation is improving but maintaining calibration among all the network stations relies on the skill and diligence of the Central CO₂ Laboratory (CCL) and the operating laboratories.

3.2 Maintaining the WMO CO₂ Background Air Pollution Monitoring Network

The group, while realizing that it did not have the mandate to discuss station location and scientific aspects of network extension, believed that the number of CO₂ measuring sites and their location is being built up in line with existing WMO recommendations. In broad terms the extent of the network and the improved precision now being achieved are generally approaching the scientific requirements set in earlier times. With respect to measurement technique, there is now considerable confidence that further improvements in precision will be forthcoming and will enable the scientific requirements mentioned in 3.1 above to be achieved. Furthermore, it would compromise the accuracy and precision achievable in the network if the number of monitoring sites would be reduced at this stage.

- It was recommended that the participating organizations continue to operate all existing stations.

A unique feature of the WMO CO₂ network is the almost continuous record of atmospheric CO₂ obtained since 1958 at the station with the longest record, the Mauna Loa Observatory, using a NDIR gas analyzer and procedures which have remained unchanged for 27 years. The meeting recognized the value of continuing this set of measurements and procedures as long as possible as a comparator with the other measurements of the WMO network, the latter necessarily obtained with instruments which operate using the same measuring principles but somewhat varied methods. Accordingly, the group of CO₂ experts recommends:
that the Scripps Institution of Oceanography, where the Central CO₂ Laboratory is currently located, continues to operate the continuous analyzer at the Mauna Loa Observatory calibrated as closely as possible with the WMO CO₂ Primary Standards.

**4. GAS STANDARDS AND CALIBRATION TECHNIQUES**

This topic was discussed intensively by the group as a major point. The results of the discussions and recommendations are summarized in the following paragraphs.

**4.1 The role of the WMO/BAPMoN Central CO₂ Laboratory (CCL)**

The CCL was established at the Scripps Institution of Oceanography (SIO) in 1975 in accordance with recommendations of a WMO Expert Meeting held in 1975. Its principal purpose was (and is) to ensure all atmospheric CO₂ measurements of the WMO programme are referred to a common scale. This process requires the preparation of a set of primary standard gas mixtures of precisely known concentration, which remain stable for at least several years. Precision is achieved by mutually comparing these mixtures by means of the same type of gas analyzer used in the observing programmes (presently NDIR) and relating instrument response to an independent absolute method of determining gas concentration. At present absolute concentrations are determined directly on the suite of standard gases themselves using a constant volume manometer.

The U.S. National Bureau of Standards (NBS) is working with SIO to prepare standard reference materials (SRM's) in order to provide a second independent absolute method of determining concentration. This second method will give additional assurance that the concentrations assigned by the CCL have the lowest possible absolute uncertainty and, by the long-term continuance of the NBS SRM programme, will help assure permanent continuity in standardization of the WMO CO₂ programme. The NBS and SIO are seeking to understand and resolve the differences currently existing between the NBS SRM's and the manometric standards of SIO.

A Central CO₂ Laboratory, wherever located, will always be necessary in order to maintain and improve, if possible, the precision of the measurements of the WMO programme. This will still require relating field measurements to a single set of Primary Standards held at the CCL.

The specific function of the CCL should include:

(a) the maintenance of WMO Primary Reference Gases;

(b) the assignment of concentration values to the Secondary Gas Standards used in the national programmes;

(c) co-operation in the inter-calibration among national programmes;

(d) the maintenance of standardization and calibration records. In addition the CCL should seek to improve the calibration procedures and techniques, including evaluation and testing of new or improved equipment.

Additional discussion of the CCL appears in the next Section, 4.2.
4.2 Calibration standards

In the following, these definitions are used:

The WMO CO₂ Primary Standards refer to the suite of CO₂-in-air gas mixtures (presently twelve in number) kept in high pressure cylinders at the CCL for the purpose of assigning precise CO₂ concentration values to the national or regional Secondary Standards.

The national or regional Secondary Standards refer to the suite of CO₂-in-air gas mixtures (preferably four or more) in high pressure cylinders kept at national or regional laboratories for the purpose of assigning CO₂ concentrations to their own calibration gas system (Working Standards).

4.2.1 The current situation regarding calibration standards

The situation with respect to reference standards has changed greatly since the last WMO meeting in 1981. There are now two independent absolute methods that give results well within 1 ppmv of one another. The oldest method in existence is the manometric analysis method used at the SIO. In the last few years the U.S. National Bureau of Standards (NBS) has successfully developed a gravimetric method to synthesize gas standards from their high purity components. More recently, the French company L'Air Liquide (AL) and two Japanese groups have also successfully synthesized gravimetric standards. The agreement between AL and SIO in the concentration range between 330 and 355 ppmv is excellent. Details on the quality of the standards provided by L'Air Liquide, and on the results of an intercomparison with the SIO are given in Annex IVC. The agreement between SIO and NBS in the range 340 - 375 is also excellent but a disagreement exists at the 304 ppmv level.

The group heard a detailed discussion of the history of the WMO CCL now at SIO, in calibrating standard gases by the manometric method. Especially in recent years, partially because of the intercomparisons with NBS, new aspects have emerged. The original agreement between NBS and SIO which was observed in 1982 in the range 335 - 355 appears, after cleaning of the Scripps manometer and readjustment of the SIO 1982 values, to differ by a few tenths of a ppmv. Also, there are some other differences between NBS and SIO that need further explanation. These differences suggest problems may still be present in one or both of the methods. The group therefore recommended strongly that:

- NBS and SIO should continue their ongoing efforts to uncover the nature of the existing discrepancies and bring their standards into accordance.

The group recognized the availability of reliable absolute standards from the NBS and recommended

- the orderly integration of these standards into the WMO CO₂ measurement programme and that the NBS responds to the documented need for expansion of the current series of standards.

However because of the complexity and diversity of the calibration system currently employed by the various national laboratories, the group does not recommend at this time that NBS constitute the sole source of absolute standards. The group recognized that several years will be required to integrate the proposed expanded series of NBS SRM's into the system.
The group identified two distinct aspects to the role of standard gases in the CO$_2$ measurement programme. First, it is highly desirable that measurement programmes strive to determine the actual mole fraction of CO$_2$ in air as accurately as possible. Second, in addition to absolute uncertainty it must be possible to measure temporal and spatial variations to a level of precision substantially better than what is achievable in an absolute sense. Continuation of the CCL is essential to maintain or improve the precise intercomparability of the various measurement programmes (laboratories) within the WMO network. The CCL maintains a set of primary standards (CO$_2$-in-air), to which all other standards are referred. This provides the common scale to all participating laboratories that allows for more precise intercomparisons than can be achieved by absolute methods alone. To do otherwise would be a significant step backwards.

With regard to absolute uncertainty, the group recommended that:

- NBS produces an SRM with a concentration in the vicinity of 360 ppmv;
- NBS provides SRM’s in tanks with a capacity of at least 5 m$^3$ (about 150 cf);
- new SRM's be issued that stay ahead of the increasing maximum atmospheric background levels, preferably at intervals of 5 to 10 ppmv;
- other groups that are preparing absolute standards intercompare their results with the CCL and provide a range of gases between 330 and 370.

With regard to precision the group recommended that:

- the CCL continue to provide calibrations of the national Secondary Standards sent to it by other laboratories with reference to the suite of Primary Standards it maintains. The time required to carry out these calibrations should not be over two months;
- the CCL acquire the most advanced gas analyzer instruments available and employ these instruments to improve the precision of the WMO CO$_2$ Primary Standards;
- the CCL works vigorously to improve the precision of the Secondary Standards with respect to the WMO CO$_2$ Primary Standards;
- the suite of Primary Standards be checked regularly by absolute methods;
- a plan be developed by SIO under WMO auspices for the long-term continuance of the responsibilities of the CCL or for the transfer to another laboratory;
- the various national or regional programmes establish their own suite of laboratory standards (referred to as National Secondary Standards) which should be sent periodically to the CCL for comparison with the WMO Primary Standards. (This set of National Secondary Standards will be used to maintain a local calibration system. The national programmes may consult with CCL for advice on procuring such gas mixtures if not readily available.)
all laboratories report their CO₂ concentrations in the WMO Provisional 1985 CO₂ Calibration Scale as defined in Keeling et al. (1985, see Annex I, p. 5).

4.2.2 Report of the CCL

The group was informed in detail about the activities of the CCL, in particular about repeated measurements on sets of CCL and NBS prepared calibration standards both CO₂-in-air and CO₂-in-N₂, which were measured by the constant volume manometer and the NDIR analyzer which have been used for many years. The written report, submitted as a formal report to WMO, will be published in the Environmental Pollution Monitoring and Research series as a separate report. A summary of it, prepared by Dr. C.D. Keeling after the meeting, is attached as Annex I.

4.2.3 Report of the U.S. National Bureau of Standards

The representatives of the NBS informed the group that in response to a recommendation of the 1977 Conference on Global Effects of Carbon Dioxide from Fossil Fuel, the NBS made efforts to develop stable SRM's of CO₂-in-air with a total relative uncertainty of 0.1 % or less at the 95% confidence level. Consequently, the NBS had developed and issued seven such SRM's at four different nominal concentrations.

The concentration in each cylinder of SRM's is certified to be accurate to within 0.2 ppmv (95 % confidence limit) for a period of at least two years. NBS presently has a suite of about 50 gravimetrically prepared primary standards of CO₂ in air, covering the range 290 - 380 ppmv. Primary standards in this set have shown no change in CO₂ concentration since their preparation (covering a period in excess of five years). The SRM's, generally comprising a batch of fifty simultaneously prepared cylinders, are certified for CO₂ concentration by analytical intercomparisons with the gravimetric primary standards maintained by NBS.

The seven currently available SRM's are in aluminum cylinders at pressures of about 12 to 14 MPa and are certified by gravimetry. The approximate CO₂ concentrations (ppmv) and the content (at STP; in m³ shown in brackets) are:

335 (0.85), 342 (0.85), 351 (0.85), 341 (4.25), 341 (0.85), 375 (4.25) and 375 (0.85).

Two CO₂-in-air SRM's currently are being made ready for certification at a nominal CO₂-in-air concentration of 300 ppmv and will be available in 1986 in 4.25 m³ and 0.85 m³ sizes. The NBS position with regard to CO₂ SRM's was summarized as follows:

a) The NBS, as evidenced by its development of SRM's of CO₂-in-air for use in the calibration of global measurements of atmospheric CO₂, has a committed long-term interest in supporting the needs for calibration standards of the WMO community involved in such measurements. As long as these needs exist, the NBS will continue to provide accurate, stable SRM's of CO₂-in-air. Furthermore, as atmospheric concentrations of CO₂ continue to increase in future years, it is the intention of NBS to replace lower concentration SRM's of limited interest with new SRM's at higher concentrations to provide a standards set that will continue to bracket the atmospheric concentration range of interest.
b) One important operational aspect of NBS SRM's is worth noting. (The sales of SRM's are managed under a self-perpetuating, non-profit recycling budget programme to restock SRM's that are sold.) Once an SRM is in place, it does not require additional external funding to ensure its long-term availability, and it will continue to be available as long as the need for it exists. As long as NBS exists, accurate and stable CO₂-in-air SRM's will be available to serve the measurement calibration needs of the WMO global atmospheric CO₂ monitoring community.

After this meeting, the NBS prepared a statement which describes the NBS response to the discussions and recommendations of the meeting and other NBS CO₂ SRM activities. It is attached as Annex II.

4.3 Intercomparison tests of national laboratory calibration scales

In 1984–1985 an attempt was made to intercompare the national laboratories CO₂ calibration scales. Although this planned experiment met with enthusiastic response from all international CO₂ laboratories, unfortunately it had to be terminated. This was due to the fact that all three gas cylinders being circulated were leaking. The intercomparison was also proceeding more slowly than required.

Despite this setback it was agreed that an intercomparison can and should be performed and that the unfortunate experiences mentioned before can be avoided in future. Furthermore, the proposals above, that national laboratories maintain their own scales, gives greater importance to the need for intercomparing these scales. Laboratories just beginning CO₂ programmes are also encouraged to participate in the intercomparison. Such laboratories should contact the WMO Secretariat.

The group specifically recommended that:

- the NOAA/GMCC group co-ordinate a new intercomparison between national laboratory scales. The WMO, NBS and AES (Atmospheric Environment Service, Canada) have each indicated a willingness to assist with the provision of cylinders for this purpose;

- three sets each of three gas cylinders should be prepared and each set circulated to approximately one third of the participating laboratories and then returned to the co-ordinating group. After completing a circuit in this way, each set of cylinders should be rotated around a new group of participating laboratories so that all laboratories eventually receive all nine cylinders;

- the coordinating group is requested to establish a definite timetable for the arrival and departure of each set of gases at all participating laboratories. Furthermore, investigations should be made regarding the most efficient means of transportation;

- the cylinders should be supplied with pressure regulators and if practical with adaptors suitable for gas fittings in use by the national laboratories. Laboratories should analyze the cylinders with the regulators supplied and may as an option analyze them with locally supplied regulators as well. In the latter case both numbers must be furnished to the co-ordinating group;
the three cylinders in each of the three sets should have concentrations close to 335, 345 and 355 ppmv;

participating laboratories should determine their best estimate of the cylinder CO₂ concentrations treating them as tertiary field standards and using their national calibration scale or equivalent. The results should be expressed on the same scale normally used to report ambient air data. The measured CO₂ concentrations should be reported to the nearest hundredth ppmv to both the WMO Secretariat and the co-ordinating group;

participating laboratories should not attempt to use the intercomparison cylinders to establish a national laboratory scale. In particular, the laboratory should have previously acquired CO₂-in-air Secondary Calibration gases calibrated at the WMO CCL;

participating laboratories are urged to handle the intercomparison gas cylinders with the utmost urgency. In particular, they should make their best endeavours to meet the timetable set for transport of the cylinders and notify the co-ordinating group in the event they are unable to meet the timetable. In this case they may be required to forward the cylinders without making an analysis;

participating laboratories, prior to forwarding the cylinders, should confirm with the next laboratory in the rotation cycle that they are prepared to receive them and agree on the means of transportation to be used. In the event that the next laboratory is not ready to accept them, the laboratory holding the cylinders should immediately notify the co-ordinating group who will be responsible for alternative arrangements. In any case the tanks should be returned to the coordinating laboratory if the pressure in the tanks is less than 3.5 MPa;

in view of the urgency of maintaining the rotation of the cylinders, all participants should communicate by telephone and/or by telex or telegramme. In countries where an office exists of a Resident Representative of the UNDP (United Nations Development Programme), this office, in coordination with the WMO Secretariat, should be requested to arrange for the settlement of administrative problems that may appear;

the coordinating group should carry out a thorough analysis of the results. These will be provided to each participating laboratory and to WMO, who will publish the report.

5. FIELD MEASUREMENTS AND ANALYTICAL TECHNIQUES

5.1 Reports on national CO₂ monitoring programmes

The participants reported on the current status of their national CO₂ monitoring activities within BAPMoN and national programmes. Reports were presented by experts from Australia*, Canada*, the Federal Republic of Germany, France*, Italy, New Zealand, Peru, Spain and the U.S.A.*. Representatives from China and the Republic of Korea informed the group on future plans in joining the BAPMoN CO₂ monitoring community. A joint report for the Federal Republic of Germany and Spain (on the Izaña global BAPMoN

* reports are attached as annexes IVA –IVD.
station) and the report for Peru (global BAPMoN station Huancayo/Cosmos) because of their length will be published in the WMO Environmental Pollution Monitoring and Research Programme report series.

5.2 Improvement in NDIR instrumentation and gas sampling procedures

The CCL and several national laboratories showed evidence of recent improvements in the precision of CO₂ analysis by non-dispersive infrared (NDIR) gas analysis and there was optimism concerning future improvements in view of the Japanese results. These were supported by preliminary laboratory studies in Australia. Possible causes of recent and anticipated improvements include:

a) the utilization of high precision signal processing which has been incorporated into a number of existing measurement systems (see Section 5.2.1);

b) general improvement in electronic control of power supplies, temperature regulation, etc.;

c) the use of infrared optical filters and the avoidance of inefficiencies in the conditioning of gas streams;

d) the attention to the regulation of the temperature and handling of gases before entering into the NDIR analyzer.

5.2.1 Electronic data acquisition

In addition to uncertainties related to electronic noise, temperature flow, and interference from water vapour, one factor affecting the precision of NDIR measurements of CO₂ is the precision with which the analyzer output (voltage) signal can be measured. During the 1950's and the 1960's the analyzer signals for ambient air and standard gases were logged as a pen trace on a strip chart recorder. The difference between the trace for the standard and the trace for the air was then measured by hand and scaled to give the CO₂ concentration for air. This method is limited by the imprecision in hand measurement (approximately 0.1 ppmv) and by systematic differences between individuals making the measurements.

A significant improvement in the precision of CO₂ measurements has been achieved through the implementation of instruments to convert the analogue output to precise digital values. These values together with the strip charts should be retained as the primary data base. This method of data acquisition has reduced one component of the overall CO₂ measurement uncertainty from about 0.1-0.2 ppmv to the level of a few hundredths of a ppmv.

5.2.2 Conditioning of gas streams

The group emphasized that in addition to improvements in analyzer design two other areas require further attention if the current levels of precision are to be improved: the removal or adjustment of water vapour in the sample in order to minimize its effect on the analyzer signal, and the temperature conditioning of the gas streams before entering the analyzer.
The removal of water vapour from the sample air prior to measurement in the analyzer is considered to be essential. For analyzers that use a 4.2 micrometre infrared filter this may not be as critical, although it was noted that such filters cannot correct for the error caused by the direct effect of the presence of water vapour on the CO₂ density.

The group discussed how each laboratory dried their samples with respect to the designs of freeze traps used and whether or not additional chemical drying was used. All laboratories assumed that the air passing through the cryo-trap did, in fact, cool to the temperature of the refrigerant and that the resulting vapour pressure was the saturation vapour pressure at the temperature of the trap. The group expressed concern regarding the effectiveness of the cryo-traps, especially after cleaning. No laboratory had experimental evidence to show that the air stream did cool the gas to the trap temperature, although SIO stated that they could detect no change in their analyzer response when multiple traps were used. NBS described a cryo-trap design which had been in use in their laboratories and which they considered to be very effective, down to 1 ppmv H₂O (see Figure in Annex VI). In the trap, filtering the air with glass wool was considered to be necessary to prevent ice crystals that could form in the air stream from leaving the trap. Knowing that there is a degradation in the effectiveness of the cryo-trap as the coolant becomes contaminated by ambient humidity, the French CFR (Centre des Faiblesses Radioactivités) institute empirically determined a CO₂ correction factor linked to the temperature of the bath and applied it to the New Amsterdam continuous analyzer (URAS 2T) data. This correction was determined in the following manner. A dry standard gas (air carrier gas) of predetermined concentration was moistened by flowing it through water, which had been previously saturated with CO₂, then through the cold trap at a selected temperature. By alternately passing the moisture conditioned gas and the dry gas through the analyzer, the efficiency of the trap at various temperatures up to -30°C had been determined. The bath was renewed as soon as the temperature reached -35°C. It should be noted that no correction has to be applied from -65°C to -55°C, while correction increased to 0.4 ppmv at -35°C:

<table>
<thead>
<tr>
<th>bath temperature</th>
<th>-65</th>
<th>-60</th>
<th>-55</th>
<th>-50</th>
<th>-45</th>
<th>-40</th>
<th>-35</th>
<th>-30</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppmv CO₂ correction</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.05</td>
<td>0.12</td>
<td>0.23</td>
<td>0.36</td>
<td>0.50</td>
<td>ppmv</td>
</tr>
</tbody>
</table>

As recent work by Tanaka et al. (1983) indicates, water vapour can also cause drift in CO₂ concentrations in flask samples. The group recognized that this is a potentially serious problem requiring further study.

Because the NDIR technique is essentially a density measurement, temperature differences between the sample and reference gas streams of 0.1°C will give rise to measured concentration differences of approximately 0.1 ppmv. These temperature differences will critically limit any improvements in precision due to improvements in analyzer electronics. The group therefore recommended, that individual groups evaluate the likely influences of differences between the temperature of sample and reference gas streams on the variability and accuracy of their measurement systems.
A different way of water vapour conditioning was reported as used by some stations, e.g. at the BAPMon stations operated by the German Federal Environmental Agency. A device placed within a small refrigerator (gas cooler) and typically kept at precisely 4°C ± 0.2°C humidifies the sample or calibrating gas in a bubbler at pH=4. Then, the gas runs through two cooling coils to remove the water vapour and adjust the temperature. Within a very large range of water vapour content of the sample air no change on the analyzer signal is measurable with the sensitivity set to 50 ppmv full range. Care is also taken to prevent back diffusion of water vapour from inside the laboratory through the gas outlets of the analyzer system.

Recognizing that the procedure is less expensive than cryo-trapping and works quasi-continuously, the group proposed that this procedure be carefully compared experimentally with the cryo-trap procedure.

5.3 Atmospheric CO₂ isotopes and other isotopic tracers

The representative of the Institute for Environmental Physics (University Heidelberg, Federal Republic of Germany) reported on this topic. Long term measurements of Carbon (¹³C, ¹⁴C) and Oxygen (¹⁸O) isotopes made in addition to CO₂ concentration observations provide essential additional information on the global carbon cycle, particularly on the identification of sources and sinks (e.g. biogenic, oceanic and anthropogenic). In recent years, several different institutions have started or will start national programmes on isotopic monitoring at various stations.

Different sampling techniques have been used: flask sampling, cryogenic trapping, in-situ cryogenic trapping and chemical absorption. All laboratories refer to one or more internationally recognized carbonate standards (e.g. the PTB = Physikalisch Technische Bundesanstalt, Federal Republic of Germany, standard) for ¹³C analysis, and NBS oxalic acid for ¹⁴C. However, no intercomparisons with air standards have been done up to date. The working group recommended:

- The enlargement of the Carbon and Oxygen isotope monitoring network;
- the setting up of a Central CO₂ Isotope Laboratory. This laboratory should keep several (at least four) Primary Standards (CO₂-in-air) for future intercalibration;
- the preparation of a number of CO₂-in-air samples by this WMO Central CO₂ Isotope Laboratory and their distribution to all national isotope laboratories for a first intercalibration.

As has been illustrated by several recent studies simultaneously observing atmospheric trace constituents like ²²²Radon and ⁸⁵Krypton provide helpful additional information for the interpretation of the observed CO₂ concentration records. The group therefore recommends that

- additional isotope observations be carried out which may lead to a better understanding of the CO₂ cycle;
- where possible isotopic measurements be complemented with measurements of other trace constituents, e.g. ²²²Radon and ⁸⁵Krypton.
The group was also informed about present international isotope monitoring activities for which the following list was presented:

<table>
<thead>
<tr>
<th>Country</th>
<th>$^{13}$C</th>
<th>$^{14}$C</th>
<th>$^{18}$O</th>
<th>$^{222}$Rn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
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<td>Switzerland</td>
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<td>U.S.A.</td>
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<td>x</td>
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</tbody>
</table>

(1) $^{13}$C and $^{18}$O to start in 1986

6. SCRUTINIZATION, REPORTING AND PUBLICATION OF DATA

6.1 Data comparability

The 1981 WMO CO$_2$ expert meeting on CO$_2$ measurement suggested that with conversion to CO$_2$-in-air reference gases and adequate attention to instrument calibration an interstation network precision of 0.2 – 0.3 was probably attainable. Annex IVD, p. 5 shows annual mean atmospheric CO$_2$ concentrations vs. latitude for several (global background) sites at which continuous analyzer or flask sample measurements are made by a variety of laboratories. These figures are intended to provide a summary of the development of interstation network precision from 1981 – 1984. It should be noted that observations from continental type stations were not considered in any year.

In 1981 the latitude gradient shows considerable scatter, particularly in the southern hemisphere where differences of 1 to 2 ppmv are observed between sites at similar latitudes. In the equatorial region and in the northern hemisphere differences of about 1 ppmv are observed even between measurements made by different laboratories at the same site.

In 1982 there is a marked reduction in the scatter, especially noticeable in the southern hemisphere, although a difference of about 1 ppmv is observed between sites at 41°S and 43°S. 1983 shows even more coherence in the southern hemisphere with differences less than 0.5 ppmv between stations at similar latitudes. More scatter is observed in the tropics and northern hemisphere, but measurements at the same site by different laboratories agree to better than 0.5 ppmv.

In 1984 the overall interstation precision is the best obtained to date. Several sites with overlapping measurements show agreement of 0.2 ppmv or better. The equatorial and southern hemisphere maxima are well defined by data from a variety of national programmes. There are, however, sites with differences of 0.5 to 1.0 ppmv.
In viewing these plots it is important to remember that differences between sites at similar latitudes but different longitudes may be due to actual longitudinal gradients. These gradients are probably greater in the northern hemisphere. On the other hand, the low scatter in 1982 may be in part fortuitous due to the anomalous transport conditions associated with the 1982/83 El Nino southern oscillation.

The participants agreed that significant progress has been made in attaining the interstation network precision suggested in 1981. As measurement techniques continue to improve it is important that the network precision also improves so that small differences between sites can be interpreted. The improvement in network precision will require continued vigilance on the part of each laboratory and the CCL with regard to measurement precision and close co-operation among the laboratories to improve and standardize sampling and analytical procedures.

6.2 Data reporting

The participants noted that the prompt reporting of provisional CO₂ measurements recommended by the 1981 meeting, has been very useful to the CO₂ community. Since 1982, WMO has prepared annual reports of these provisional data. The participants agreed that these WMO publications should continue under the same guidelines recommended in 1981, with some modification (see below). Scientists from all national programmes should continue to submit current and revised past data. The data for each calendar year should be submitted if possible as camera-ready copies to the WMO Secretariat by December 31 of the following year. The Secretariat will promptly compile and publish these data and transmit them to all participating and interested organizations.

The participants agreed that, for in situ measurements, daily averages of data selected to represent background conditions should be published. For discontinuous (i.e. grab or flask sampling) measurements, all valid (not instrumentally in error) data should be reported, but values not representative of background conditions should be flagged as such. "Background conditions" will not necessarily be defined equally at all stations. The WMO published reports should include an information page from each institution with the following: Author; organization; address; site position and description; sampling method and frequency, and measurement technique; scientific aims and scope of measurements; data selection procedures used; calibration gases used; scale of reported data; literature reference to programme; and (if needed) explanatory notes.

With regard to the Provisional Data Reports the group proposed that every year each cooperating organization responsible for a CO₂ measurement programme should prepare a brief report containing daily averages in a standard format for each measurement station summarizing the previous years data in line with the example in Annex V. The reports should be submitted as soon as possible during the year following the report year to the WMO Secretariat, who will be responsible for their joint publication and circulation to all cooperating organizations. The group recommended the following modifications to the format of the report:
Measurements from in-situ analyzers should be reported to the nearest hundredth ppmv for data since 1984. For earlier periods each laboratory may report to the nearest hundredth or tenth ppmv.

Each institution should include at the bottom of each page a statement: "The hundredth digit of CO₂ concentrations may not have significance."

Each institution should include at the top of each data page a statement whether the data are "PROVISIONAL", "CORRECTED" OR "FINAL".

Each institution should include at the top of each data page a statement giving the date (month and year) the data were prepared for this publication.

Grab sample measurements should be reported as daily averages to the nearest tenth ppmv on the same format as in-situ data. All values not judged to be representative of background conditions should be identified (flagged) with a symbol, to be defined at the bottom of the page. An example is shown in Annex V.

6.3 Data scrutiny, selection and assessment

As the CO₂ data become more precise, problems of converting the data to monthly and annual averages will increase in significance. Different groups use different criteria for example, to select background data, to interpolate for missing data or to extract information on monthly averages and annual cycles. Therefore, the group recommended that the WMO convenes a meeting of a group of experts to discuss ways of perfecting the procedures. Recognizing the importance of this problem in interpreting time series of CO₂ and other atmospheric constituent data, the group recommended that this workshop should be held within not more than two years time.

7. CLOSURE OF THE MEETING

In their closing remarks the host, Professor Dr. Charles D. Keeling, and the WMO representative, Mr. Albert Köhler, thanked the two chairmen for their excellent work, all participants present in the conference room or working behind the scenes for their engaged contributions or their valuable assistance in implementing the meeting. Also, the activity of WMO and the CCL were especially appreciated by the experts present. After the formal closure at Lake Arrowhead, those who were interested were offered a guided tour through the CCL at the Scripps Institution of Oceanography, La Jolla.
MAINTENANCE OF WMO PRIMARY AND SECONDARY STANDARDS
BY THE CENTRAL CO₂ LABORATORY

Prepared by Charles D. Keeling and Peter R. Guenther.
Scripps Institution of Oceanography
La Jolla, California 92037, USA

1. Introduction

Since the meeting of experts on instruments, standardization and measurement techniques for atmospheric CO₂ in Geneva, Switzerland during September 1981, the Scripps Institution of Oceanography Central CO₂ Laboratory (CCL) has carried out two major calibrations of primary reference gas standards. Measurements were made both with a constant volume manometer and with a nondispersive infrared gas analyzer. The first of these calibrations, in 1983, resulted in a provisional manometric scale reported by Keeling et al. (1984). The second resulted in a final manometric scale for all calibrations carried out before 1 August, 1985 (Keeling et al., 1985). This new scale was discussed at the Lake Arrowhead meeting in November, 1985, and adopted for reporting atmospheric CO₂ data for the WMO Environmental Pollution Monitoring Programme.

Soon after the Lake Arrowhead meeting the CCL redetermined the volume of one of the chambers of the constant volume manometer in order to confirm the absolute calibration of the new 1985 scale. The relevant data and the significance of this determination are discussed by Guenther and Keeling (1986). Their report, and the report by Keeling et al. (1985), will be issued as part of the technical series of the WMO Environmental Pollution Monitoring Programme. The principal results of these calibrations are discussed in this annex.

The CCL, in addition to maintaining primary standards, calibrates gas mixtures for organizations participating in the WMO Environmental Pollution Monitoring Program. These mixtures, called secondary standards, are directly intercompared with intermediate standards of the CCL which, in turn, are calibrated against the primary standards. The CCL is able to prepare such standards de novo or to calibrate existing reference gas mixtures of other laboratories which thereby become WMO secondary standards. The reliability of these standards is also discussed in this annex.

2. Precision of Primary Standards

The CCL maintains two sets of primary standards. One set consists of 11 gas mixtures of CO₂-in-nitrogen in the range of 196 to 473 ppm (parts per million by volume). The other set consists of 12 mixtures of CO₂-in-air in the range 101 to 503 ppm. The CO₂-in-nitrogen set was put in service in 1974 and has been the basis of determining the stability of a system of intermediate standards used at the CCL to prepare secondary standards for the WMO programme. The CO₂-in-air set was put in service in 1981. This set establishes a direct scale for air, as discussed below.

During the 1983 and 1985 calibrations at the CCL, all primary standards were measured manometrically (Keeling et al. 1985). All but the CO₂-in-air standard of lowest concentration were also intercompared with the CCL Applied Physics Corporation (APC) non-dispersive infrared (NDIR) Gas Analyzer. These NDIR intercomparisons occurred during intensive calibration exercises in which all gases were compared over a 24 hour period, in sets of ten intercomparisons each, against three intermediate standards. The calibrations were spaced over
approximately 2 months each year.

The imprecision of the results is summarized in Table 1. The standard deviations of a single manometric measurement and a single set of ten intercomparisons by NDIR analysis vary only slightly from year to year. For the 1983 and 1985 data combined, the corresponding standard deviations are 0.064 ppm by manometric analysis, 0.142 ppm by NDIR analysis. The standard deviations in the means therefore are 0.032 ppm and 0.045 ppm, respectively, where 4 analyses contribute to each manometric deviation and 10 sets of intercomparisons to each NDIR deviation. The corresponding response curves of the NDIR analyzer for the CO₂-in-nitrogen and CO₂-in-air standards, determined by least squares fits to cubic power series in NDIR response (expressed as a CO₂ index), yield standard errors of the predicted manometric concentration of 0.047 ppm and 0.066 ppm, respectively (Guenther and Keeling, 1986, Table 10). These values agree closely with the root mean square of the sums of the above quoted standard deviations of replicate manometer and NDIR measurements (0.056 and 0.054 ppm, respectively). The large number of standards involved in the fits offers considerable assurance that the response curves are valid within the computed statistics.

3. Precision of Secondary Standards

The estimated standard deviation for a single set of ten NDIR intercomparisons (0.142 ppm) has been derived for NDIR analyses in the concentration range 196 to 503 ppm. One might expect that the statistical errors for NDIR analysis when calibrating secondary standards for the WMO programme should be smaller because the calibration range is typically only 300 to 380 ppm. This prediction, however, supposes that the instrument response curve during routine calibrations is established equally as well as during intercomparisons of primary standards. This is not necessarily the case, and the precision of secondary standards needs to be verified, as now discussed.

In order that the CCL primary standards not be depleted in a short time, they are analyzed only during major calibration exercises, one or two years apart. On these occasions three intermediate standards are included in the NDIR analysis procedure. These standards are also the basis, at other times, for calibrating secondary standards for the WMO programme. The intermediate standards sometimes became depleted between major calibration exercises and were replaced by additional intermediate standards calibrated against them by NDIR analysis. All of the data used to maintain these intermediate standards are compiled in reference gas reports (now 50 in number) kept at the CCL. It is important to know how well the performance of these intermediate standards is reflected in the preparation of secondary standards.

This performance is illustrated by data in Table 2. Here are shown calibrations of four SIO gas mixtures of CO₂-in-air specifically introduced into the calibration procedures of the CCL to test the methodology of preparing secondary standards. These special surveillance secondary standards each received two manometric analyses in 1982 and extensive NDIR analyses each year from 1981 through 1985. Three of these mixtures, having concentrations of CO₂ close to or somewhat below that of air, show a standard deviation of a single set of ten NDIR intercomparisons of 0.094 ppm. For one gas mixture well above air concentration the standard deviation is considerably larger (0.297 ppm).

The standard deviations of secondary standards by NDIR analysis are expected to increase in proportion to their concentration difference from that of air, because the three intermediate CCL standards are themselves chosen to have concentrations in a narrow range between approximately 330 to 360 ppm (Bacastow et al., 1983a). The NDIR analyses for the highest concentration mixture in Table 2 involve considerable extrapolation from the concentration range of the intermediate standards.

Extrapolation could, of course, be overcome by using intermediate standards with a wider concentration range, but this would require additional intermediate standards or would compromise the calibration of secondary standards with concentrations near that of air. Since the concentrations of most of the secondaries prepared for the WMO programme are nearly within the range of the intermediate standards, we have maintained this range up to now.
The statistical uncertainty in the mean concentrations from NDIR analysis can be made small by making a sufficient number of intercomparisons. For example, for 10 sets of 10 intercomparisons for the highest concentration gas mixture in Table 2 the standard deviation in the mean is predicted to be:

\[ 0.297/10^{1/2} = 0.094 \text{ ppm} \]

For precise standardization the CCL, indeed, recommends 10 sets of comparisons. Where less precise standards are acceptable, the CCL recommends 5 sets. It can be seen that even this fewer number is sufficient to produce a standard deviation of the mean for the other three gas mixtures in Table 2 significantly below 0.10 ppm.

That repeated NDIR calibrations do, in fact, result in stable data is demonstrated by the agreement of averaged NDIR data for different years, as shown in Table 3. Annual averages show no evidence of systematic drift in concentration. Furthermore, the means for all four mixtures agree closely (within 0.05 ppm) with manometric analyses. This indicates that significant biases were not introduced into the calibration of these secondary standards by the procedures used to relate them to the primary standards via the intermediate standards.

A direct illustration of the performance of the CCL to prepare secondary standards for the WMO programme is given by a second set of data in Table 2 for five standards prepared by the U.S. National Oceanic and Atmospheric Administration (NOAA) and analyzed by the CCL in 1982. Although not a normal procedure for secondary standards, in this instance manometric analyses were also made. If the data for all gas mixtures are combined, the standard deviation of an individual set of NDIR intercomparisons is computed to be 0.096 ppm. The means for individual mixtures differ from the manometric analyses on average by 0.08 ppm, the manometric data being higher. These differences themselves have a standard deviation of 0.060 ppm, consistent with a statistical prediction based on replicate NDIR and manometric analyses:

\[ \left(0.096^2/6 + 0.064^2/2\right)^{1/2} = 0.060 \text{ ppm} \]

where the standard deviation of a single manometric analysis is taken to be 0.064 ppm (see Section 2) and each NOAA standard received two manometric analyses. The overall bias of 0.08 ppm with respect to direct manometric analyses is larger than for the four SIO gas mixtures of Table 2, but still hardly significant.

The NOAA standards received these NDIR and manometric analyses in 1982 during a special calibration exercise involving the four SIO surveillance gas mixtures listed in Table 2. Since the results therefore may not be representative of routine calibrations, another example of the preparation of secondary standards is presented by data in Table 4 for 14 secondary standards recently prepared for the Atmospheric Environment Service (AES) of Canada. Each gas mixture was analyzed on 6 or 7 occasions between May and September, 1984. The weighted root mean square of the standard deviations of the individual mixtures is 0.097 ppm, essentially the same as for the NOAA standards. Based on these results, which accord with similar data for other secondary standards, it may be concluded the standard deviation of a single set of NDIR intercomparisons of secondary standards prepared by the CCL is approximately 0.10 ppm in the range 320 to 360 ppm. This imprecision holds for analyses carried out over only a few months (NOAA and AES secondaries) or over several years (SIO surveillance secondaries).

Thus, for secondary standards in the range 320 to 360 ppm which receive 5 sets of intercomparisons, the means of the NDIR analyses are predicted to have a standard deviation of

\[ 0.10/(5)^{1/2} = 0.045 \text{ ppm} \]

while those that receive 10 sets of comparisons should have an imprecision of 0.032 ppm. Since the laboratories of the WMO CO₂ programme have NDIR analyzers with similar performance to that of the CCL laboratory, these laboratories should be able to achieve imprecisions of the order of 0.04 ppm for tertiary standards prepared by intercomparison with secondary
standards. The combined imprecision with respect to the CCL primary system should then be of the order of:

\[ 0.04(2)^\circ = 0.06 \text{ ppm}. \]

For field studies calibrated with CCL secondary standards it should therefore be possible to establish concentration differences measured by different laboratories to within 0.10 ppm.

4. **Mole Fraction Scales of the CCL**

An important feature of the CCL calibration procedures is the updating of data for secondary standards when new calibrations are made of the primary standards. This is accomplished by expressing NDIR intercomparisons data in the form of a CO₂ index which is linearly related to the response of the APC-NDIR analyzer used for all infrared analyses of the CCL. These index values are computed only once, by interpolation from the three intermediate standards in current use. The index values of two of the latter were initially set in 1959 via manometric analysis and then repeatedly updated by comparing new intermediate standards with older ones. By precisely intercomparing successive intermediate standards, the imprecision of secondary standards, prepared at different times, is kept at a minimum. Prior to 1983, as discussed by Bacastow et al. (1983a), the index values of the system of intermediate standards (in that report called "principal" and "span" standards) drifted downward slowly with time, relative to the manometric analyses. This drift was evidently owing to small systematic biases which occurred when new intermediate standards were calibrated from older ones; it is corrected for by successive manometric calibrations, as described by Bacastow et al. (1983a).

The entire system of intermediate standards has always employed CO₂-in-nitrogen gas mixtures on the assumption that they would be more stable than CO₂-in-air gas mixtures when stored for many years. Since the response of NDIR analyzers for CO₂ is different when nitrogen replaces air as a carrier gas, it has been necessary to apply a carrier gas correction when secondary standards of CO₂-in-air are intercompared to intermediate standards of CO₂-in-nitrogen.

In 1974 a first provisional manometric mole fraction scale was adopted by the WMO programme as reported by Keeling et al. (1976). The CCL devised this scale by relating index values to manometric data via a response curve based solely on CO₂-in-nitrogen primary standards. A carrier gas correction, defined as a constant factor multiplying the CO₂ index at atmospheric pressure, was determined from manometric calibrations of a set of CO₂-in-air standards in a narrow concentration range close to that of air. Between 1974 and 1980 it was assumed that the rate of drift in the system of intermediate standards was the same as the average determined before 1974. NDIR analyses expressed using this extrapolation procedure were also designated as being on the 1974 manometric scale. In 1980 a second provisional manometric scale was adopted which updated this scale (Bacastow et al., 1983a). Because the response curve for CO₂-in-nitrogen standards of 1980 was deemed better than that of 1974, it was substituted for the 1974 response curve for all previous calibration periods. A revised carrier gas correction was also made, and the correction for system drift was revised for the period between 1974 and 1980.

In 1981 the CCL completed the preparation of a set of 12 CO₂-in-air standards over a wide concentration range. These were intercompared by NDIR analysis, and a response curve was computed on the basis of manometric analyses. The standards were also intercompared with a subset of the CO₂-in-nitrogen primary standards. A new 1981 mole fraction scale was defined (Bacastow et al., 1983b) and adopted that year by WMO. This scale retained all of the features of the 1980 scale, except for an update of system drift to 1981, and the substitution of a new carrier gas correction for secondary CO₂-in-air standards based on a full range of CO₂-in-air standards.

In 1982 the CCL provided a further update for the period 1981-1982 called the mole fraction scale of 1982 and reported by Keeling et al. (1983).
In 1983 the full sets of CO$_2$-in-nitrogen and CO$_2$-in-air primary standards received additional manometric analyses and a detailed set of NDIR intercomparisons, as described in Section 2 above. The resulting response curves were clearly superior to earlier curves, since they were based on intercomparisons carried out together on full sets of both air and nitrogen standards. A new 1983 scale was defined which superseded previous scales for all previous calibration periods (Keeling et al., 1984).

In 1984 NDIR comparisons were made of the CO$_2$-in-nitrogen standards. This calibration resulted in an update of the system drift for 1984. The scale received only limited use and was not published as a report.

In 1985, as noted in Section 2 above, another detailed analysis of all of the primary standards was carried out, similar to that of 1983. The results for both CO$_2$-in-nitrogen and CO$_2$-in-air primary standards were highly concordant with the calibrations of 1983. There was, therefore, no advantage in revising the previous scale for calibrations made prior to the 1983 calibration, the latter defined by a central date of 17 September, 1983. Between that date and the central date of the 1985 calibration, 29 July, 1985, linear interpolation in time was used. The resulting manometric scale of 1985 was adopted by the WMO programme at the Lake Arrowhead meeting in November, 1985 and is reported by Keeling et al. (1985); it is based on full calibrational data for both 1983 and 1985 and is regarded by the CCL as a final scale for all calibrations of secondary standards made before 19 July, 1985. Except for a minor adjustment which raises all of CO$_2$-in-air standards before 17 September, 1983 by 0.01 ppm, it is, before this date, identical to the 1983 scale. Thus data reported on the 1983 scale can also be regarded as final, if the analyses of secondary standards were made prior to 17 September, 1983. The previous revisions of the CCL mole fraction scale produced changes in assigned concentrations which, after 1980, did not exceed ± 0.04 ppm in the range 320 to 360 ppm and ± 0.23 ppm in the range 260 to 440 ppm, for analyses of secondary standards carried out before the final dates of validity (central dates) of the respective reports.

CCL has several times revised its mole fraction scale to promote optimal use of its calibration data. The retrospective updating of scales is now terminated by the declaration of a final scale in 1985. On the other hand, there will remain a need to update analyses of secondary standards made after the central date of the 1985 calibration. The CCL plans to carry out its next major calibration exercise in 1987. Analyses carried out between 1985 and 1987 will be computed provisionally on the assumption that the 1985 scale still applies. Thus, the CCL recommends that organizations which employ CCL secondary standards devise procedures so that they can conveniently update their computations of atmospheric CO$_2$ field observations when a final mole fraction scale for the period 1985 to 1987 becomes available.

The methodology of the CCL differs from that of a standards laboratory such as the U.S. National Bureau of Standards (NBS) which distribute standard reference materials of CO$_2$-in-air. The latter standards are "certified" to have concentrations which are thereafter not revised unless they are recertified by being returned to the standards laboratory. Because certified concentrations are final values, such standards are simpler to use than those of the CCL, but their use does not produce the most precise measurements of atmospheric CO$_2$ because the principal purpose of certification is to set an upper limit on absolute uncertainty rather than to minimize imprecision.

5. Absolute Uncertainty of the CCL Primary Standards

The mole fraction of CO$_2$ in air is determined by the CCL by means of a constant volume manometric system which contains 6 chambers having volumes which range from 1 cc to 5000 cc. The volumes increase in approximately a geometric series with the ratio of adjacent volumes being approximately 4 to 1. The pressure and temperature of samples is determined for nitrogen or air in the largest chamber (of approximately 5000 cc). The tracer gas, CO$_2$, extracted cryogenically from that air, is measured in a small chamber (of approximately 4 cc). The mole fraction of CO$_2$-in-nitrogen or air is computed from the appropriate equations of state of the gas and from the measured volume ratio of the two chambers.
Volume ratios have been determined in two essentially independent ways. The first method requires only that the equations of state of the calibrating gases be specified. A pure gas, either CO₂, nitrogen, or argon, is introduced by expansion from an external reservoir into a given chamber. After determining its pressure and temperature, it is expanded into the next largest chamber and the volume ratio computed from the change in pressure and temperature, and the equation of state of the gas. This procedure is repeated for all pairs of chambers, and the overall volume ratio is computed as a product. The chambers with nominal volumes of 250 and 1000 cc were not constructed in tandem, as were the others. For this pair of chambers only CO₂ was used in the volume ratio determination; it was transferred to the larger chamber by sublimation with liquid nitrogen refrigerant.

As reported by Guenther (1981), the volume ratio was found by the expansion method to be 1318.2 ± 0.9 where the latter value denotes a standard error of the mean of three replicate determinations of adjacent volume ratios, one each made in 1959, 1961, and 1972.

The second method employs direct calibration of 1000 and 5000 cc chambers with water, and the indirect calibration of a set of external volumes (called plenums) with mercury for the smaller chambers. Each plenum was filled with CO₂ gas to a measured pressure close to ambient, and the gas from one plenum at a time transferred by sublimation to the appropriate chamber where its pressure and temperature were measured. In 1974 a volume of 3.7974 ± 0.00018 cc was found for the 4 cc chamber and 5015.09 ± 0.09 cc for the largest chamber, thus a volume ratio of 1320.66 ± 0.07 cc.

The equations of state of CO₂, nitrogen, and argon in the pressure range of interest were verified by expansions from the calibrated 1000 cc volume to the 5000 cc volume. The uncertainties in the densities of water and mercury used in the calibrations by the second method are insignificant contributors to error in the volume ratio determination. Nevertheless, the results of the two methods are concordant only within approximately three standard deviations of the first method, i.e. about one part in 500. The second method is clearly more precise than the first method, and as discussed below agrees closely with independent absolute calibrations by a gravimetric method. It would be worthwhile to repeat the measurements made by the first method, especially since these were made 14 to 27 years ago.

6. Calibrations of the CCL Manometer

Between 1974 and 1985 the volume ratio of the CCL manometric system appears to have changed owing to progressive fouling of the mercury used in the columns to measure pressure. The manometer was cleaned and the mercury replaced shortly before the November 1985 meeting at Lake Arrowhead. The CCL informed the meeting participants that a recalibration of the 4 cc chamber would be made after the meeting. This has now been carried out, and the results are reported by Guenther and Keeling (1986).

The 1985 volume recalibration assumes that the plenum volumes did not change since 1974. The volume of the (nominally) 4 cc chamber was found to be 3.7955 ± 0.00018 cc. The 5000 cc chamber was not recalibrated since the mercury for that chamber had not fouled. A comparison of the manometric analyses of nine primary standards of CO₂-in-nitrogen measured in both 1974 and 1985, assumed to be stable, indicates that the measured volume should have decreased after cleaning to 3.7950 cc, or conversely, assuming that the 1985 volume determination is exact, that the volume should have been found to be 3.7979 cc in 1974 instead of the measured value of 3.7974 (see p. 7 of Guenther and Keeling, 1986). On the other hand, if the two measured volumes are both correct, the primary standards evidently drifted upward in concentration by 0.13%, e.g. by 0.04 ppm for a standard gas with the CO₂ concentration of 340 ppm. Such a drift in 11 years is too small to be considered significant. It is therefore assumed that the primary standards remained stable, as well as the plenum volumes.

For the period during which the mercury in the 4 cc chamber was fouled, the volume ratio was determined as a function of time from apparent shifts in the manometric concentrations of the primary standards, attributed to changes in manometer performance rather than instability in the standards. These computations, discussed by Guenther and Keeling, (1986, p.
6) affect the definition of the 1980 and 1981 mole fraction scales because each of these was based on additional manometric analyses computed on the basis of volume ratios which did not precisely account for the real changes occurring. The computations do not affect the definitions of the 1983 and 1985 scales, however, except to the extent of a single time invariant factor. This factor arises because the 1983 scale was based on a volume ratio of 1319.61 as estimated at the time of the 1983 calibration, whereas the new calibration data indicate a value of 1319.14 in 1983. The ratio of ratios, equal to 1.000356, applies to both the 1983 and the 1985 scales because the 1985 scale is forced to be consistent with the 1983 scale for dates before 17 September, 1983.

All scales, including the 1985 scale, use a provisional value for the volume of the 5000 cc chamber of 5014.9 cc instead of the final value of 5015.09 cc, discussed above. In arriving at the factor of 1.000356, just discussed, account is taken of this final value, as well as adopting the 1985 determination of the 4 cc chamber in place of forcing the 1985 scale to agree with the 1983 scale. This factor represents a bias of approximately 1 part in 3000. For a concentration of 340 ppm, as an example, correcting for it would raise the computed concentrations on the 1985 scale by 0.11 ppm.

This adjustment has no influence on the intercomparability of programs which rely on standards from the CCL. For geochemical and geophysical studies a factorial error of approximately 1 part in 3000 is too small to justify applying a correction at this time. For purposes of comparing concentrations on the WMO 1985 mole fraction scale with independent measurements of CO$_2$ standards by other organizations, the CCL recommends, however, that the new 4 cc chamber volume determination be assumed to be correct, and that this factor of 1.000356 be taken into account.

Specifically, the CCL recommends that the 1985 mole fraction scale be adhered to as adopted in November, 1985, and that the scientific community be informed via publications that the scale is presently estimated to need a correction of 1.000356. The CCL intends to include such a statement in a special volume of papers to be published by the international journal, *Tellus*, as a follow up to the symposium of 1985 held in Kandersteg, Switzerland.

The CCL plans to carry out additional calibrations of the manometer, including redeterminations of the volumes of the plenums and of the 1000 to 5000 chambers with water. As in the case of updating the mole fraction scales, as more precise standard calibrations become available, the most exact calibration scale will be obtained, if updates of the manometric volume factor can be imposed retrospectively whenever better data become available.

7. Comparisons with Standards Independent of CCL

Since 1980 the CCL has determined manometrically the concentrations of several sets of CO$_2$-in-air gas mixtures supplied by the U.S. National Bureau of Standards (NBS), and recently has performed NDIR analyses on 4 gas mixtures prepared by the French commercial firm of Air Liquide. The gas mixtures of NBS and Air Liquide were based on gravimetric procedures.

Although the imprecision of these mixtures determined by gravimetry has been found by CCL to be too large for their use as substitutes for the secondary standards prepared by the CCL, the mean absolute differences between CCL and NBS and Air Liquide, respectively, have been found to be small. Nine NBS gas mixtures, as reported by Guenther and Keeling (1986), are $0.08 \pm 0.08$ ppm lower in concentration when determined by NBS compared to the CCL, whereas four Air Liquide mixtures are $0.06 \pm 0.09$ ppm higher, where the indicated uncertainties denote standard deviations of the mean differences.
References


Table 1. Imprecisions associated with the 1983 and 1985 calibrations of primary standards

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<th>Year</th>
<th>CO₂-in-nitrogen</th>
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<td>Std. Error</td>
<td>No. of Samples</td>
<td>Std. Error</td>
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<tr>
<td>1985</td>
<td>11</td>
<td>0.155</td>
<td>11</td>
<td>0.143</td>
</tr>
<tr>
<td>Combined**</td>
<td>11</td>
<td>0.148</td>
<td>11</td>
<td>0.137</td>
</tr>
</tbody>
</table>

*Measurements adjusted for change in volume of the 4 cc chamber of constant volume manometer between 1983 and 1985 (column 8 of Table 12 of Guenther and Keeling, 1986).

**Computed as the root mean squares of the standard deviations for 1983 and 1985.

Sources of data:
1. Table 4 of Guenther and Keeling (1986)
2. Table 5 of Guenther and Keeling (1986)
Table 2. Analyses of SIO and NOAA secondary gas mixtures of \( \text{CO}_2 \)-in-air$^+$

<table>
<thead>
<tr>
<th>Cylinder No.</th>
<th>Manometric Concentration (ppm)</th>
<th>No. of sets of Intercomparisons</th>
<th>Mean Concentration (ppm)</th>
<th>Mean Difference (ppm)</th>
<th>Standard Deviation (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIO Gas Mixtures (1981-1985)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34891</td>
<td>298.11</td>
<td>30</td>
<td>298.16</td>
<td>0.05</td>
<td>0.102</td>
</tr>
<tr>
<td>62807</td>
<td>338.57</td>
<td>33</td>
<td>338.56</td>
<td>-0.01</td>
<td>0.078</td>
</tr>
<tr>
<td>62817</td>
<td>365.58</td>
<td>33</td>
<td>365.56</td>
<td>-0.02</td>
<td>0.100</td>
</tr>
<tr>
<td>62814</td>
<td>425.19</td>
<td>29</td>
<td>425.15</td>
<td>-0.04</td>
<td>0.297</td>
</tr>
<tr>
<td>Mean difference</td>
<td></td>
<td></td>
<td></td>
<td>-0.01</td>
<td></td>
</tr>
</tbody>
</table>

Weighted root mean square standard deviation of first 3 gas mixtures combined 0.094

<table>
<thead>
<tr>
<th>NOAA Gas Mixtures (1982)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3082</td>
</tr>
<tr>
<td>3074</td>
</tr>
<tr>
<td>3091</td>
</tr>
<tr>
<td>3071</td>
</tr>
<tr>
<td>3092</td>
</tr>
<tr>
<td>Mean difference</td>
</tr>
</tbody>
</table>

Root mean square standard deviation of 5 gas mixtures combined 0.096

$^*$Infrared minus manometric concentrations

$^*$Deviation of an individual set of intercomparisons from the mean infrared concentration

$^+$All data are expressed on the 1985 scale multiplied by the factor 1321.80/1321.33 to agree with the data of Table 13 and 14 of Guenther and Keeling (1986).
Table 3. Comparison of manometric and infrared analyses of SIO secondary gas mixtures of CO$_2$-in-air

<table>
<thead>
<tr>
<th>Cylinder No.</th>
<th>Manometric Concentration (ppm)</th>
<th>Annual Average Differences (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>34891</td>
<td>298.11</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9)</td>
</tr>
<tr>
<td>62807</td>
<td>338.57</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10)</td>
</tr>
<tr>
<td>62817</td>
<td>365.58</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10)</td>
</tr>
<tr>
<td>62814</td>
<td>425.19</td>
<td>-0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6)</td>
</tr>
</tbody>
</table>

Annual mean difference (unweighted) -0.010 -0.040 0.052 -0.020 0.040
Mean difference for all years (weighted) -0.01

* Infrared minus manometric derived concentrations. The numbers of sets of intercomparisons for each year and gas mixture are shown in parentheses.
+ Same scale as in Table 2
Table 4. Infrared analyses of AES secondary gas mixtures of CO$_2$-in-air

<table>
<thead>
<tr>
<th>Cylinder No.</th>
<th>No. of Sets</th>
<th>Mean Concentration (ppm)</th>
<th>Standard Deviation* (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>76859</td>
<td>6</td>
<td>321.73</td>
<td>0.11</td>
</tr>
<tr>
<td>76847</td>
<td>6</td>
<td>322.03</td>
<td>0.08</td>
</tr>
<tr>
<td>76873</td>
<td>6</td>
<td>324.51</td>
<td>0.12</td>
</tr>
<tr>
<td>76899</td>
<td>6</td>
<td>331.79</td>
<td>0.10</td>
</tr>
<tr>
<td>76898</td>
<td>6</td>
<td>332.27</td>
<td>0.08</td>
</tr>
<tr>
<td>76895</td>
<td>6</td>
<td>336.24</td>
<td>0.07</td>
</tr>
<tr>
<td>76861</td>
<td>6</td>
<td>338.43</td>
<td>0.20</td>
</tr>
<tr>
<td>76863</td>
<td>6</td>
<td>339.70</td>
<td>0.10</td>
</tr>
<tr>
<td>76876</td>
<td>6</td>
<td>345.29</td>
<td>0.08</td>
</tr>
<tr>
<td>76837</td>
<td>7</td>
<td>349.53</td>
<td>0.14</td>
</tr>
<tr>
<td>76864</td>
<td>7</td>
<td>350.31</td>
<td>0.12</td>
</tr>
<tr>
<td>76900</td>
<td>6</td>
<td>354.76</td>
<td>0.07</td>
</tr>
<tr>
<td>76905</td>
<td>7</td>
<td>361.17</td>
<td>0.08</td>
</tr>
<tr>
<td>76978</td>
<td>6</td>
<td>361.38</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Root mean square standard deviation of 14 gas mixtures combined

* Deviation of an individual set of intercomparisons from the mean concentration

† All data are expressed on the 1985 scale
POSITION STATEMENT OF THE NATIONAL BUREAU OF STANDARDS CONCERNING THE PROVISION OF STANDARDS OF CARBON DIOXIDE IN AIR AND LONG-TERM SUPPORT OF SUCH STANDARDS FOR THE CALIBRATION OF GLOBAL MEASUREMENTS OF ATMOSPHERIC CARBON DIOXIDE

BACKGROUND:

In response to a leading recommendation of the 1977 Conference on Global Effects of Carbon Dioxide from Fossil Fuels that the National Bureau of Standards (NBS) should develop stable Standard Reference Materials (SRM's) of CO₂ in air with a relative uncertainty of 0.1 percent or less, the NBS has developed and issued seven such SRM's at four different nominal concentrations.

The uncertainty of the certified concentration of CO₂ in each cylinder of these SRM's does not exceed 0.1 percent relative at the 95 percent confidence limit, and the concentration is certified to be stable for a period of at least two years.

The NBS operates an internal quality assurance program in which cylinder mixtures that are certified as SRM's are periodically reanalyzed to assess long-term stability of existing stocks of SRM's. Purchasers of gaseous SRM's are immediately notified if any concentration changes are detected. This, however, has been very rare (one case concerning a propane SRM a number of years ago in which a slight but real change was noted), and has never been noted in the case of CO₂ SRM's. Should improved preparation techniques or the use of new measurement technology for a given type of SRM afford an improved accuracy (i.e., lower uncertainty), again, the purchasers of the particular SRM are notified. Should any question develop on a purchased SRM concerning the reliability of the certified concentration, the purchaser should contact the Gas Metrology Group at the NBS (301-921-2886). The NBS will reanalyze the returned SRM against its suite of primary gas standards at no cost to the purchaser and report its findings to the purchaser. Should reanalysis confirm any problem with the sample not caused by the purchaser, the NBS will replace the returned SRM with a new SRM.

NBS presently has a suite of over 30 gravimetrically-prepared primary standards of CO₂ in air, covering a range from about 250-420 ppm (with additional primary standards extending from 200 ppm to 1000 ppm). Primary standards in this set have shown no change in CO₂ concentration since their preparation (covering a period in excess of five years). The SRM's, generally comprising a batch of fifty homogeneously-prepared samples, are certified for CO₂ concentration by analytical intercomparisons with the gravimetric primary standards maintained by NBS.

The development of these SRM's was jointly sponsored by the U.S. Department of Energy, the lead agency for the U.S. Carbon Dioxide
Program, and the NBS Office of Standard Reference Materials. The seven currently available SRM's are as follows:

<table>
<thead>
<tr>
<th>SRM No.</th>
<th>Nominal CO₂ Concentration (ppm, by mole)</th>
<th>Proximate CO₂ Concentration (ppm, by mole)</th>
<th>Size (cu. ft.)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1670</td>
<td>330</td>
<td>335</td>
<td>30</td>
</tr>
<tr>
<td>1671</td>
<td>340</td>
<td>342</td>
<td>30</td>
</tr>
<tr>
<td>1672</td>
<td>350</td>
<td>351</td>
<td>30</td>
</tr>
<tr>
<td>2607</td>
<td>340</td>
<td>341</td>
<td>150</td>
</tr>
<tr>
<td>2608</td>
<td>340</td>
<td>341</td>
<td>30</td>
</tr>
<tr>
<td>2609</td>
<td>380</td>
<td>375</td>
<td>150</td>
</tr>
<tr>
<td>2610</td>
<td>380</td>
<td>375</td>
<td>30</td>
</tr>
</tbody>
</table>

*30 cu. ft. (ca. 0.84 m³); 150 cu. ft. (ca. 4.2 m³)

These SRM's are in aluminum cylinders at pressures of about 1700-2000 psi and were certified by gravimetry.

Two CO₂ in air SRM's are currently under certification analysis at a nominal CO₂ in air concentration of 300 ppm, and should be available in 1986: SRM 2605 (cylinder size, 150 cu. ft.) and SRM 2606 (cylinder size, 300 cu. ft.). Additional SRM plans are summarized below.

**NBS POSITION:**

The NBS, as evidenced by its development of SRM's of CO₂ in air for use in the calibration of global measurements of atmospheric CO₂, has a committed long-term interest in supporting the standards calibration needs of the WMO community involved in such measurements. As long as these needs exist, the NBS will continue to provide accurate, stable SRM's of CO₂ in air for this purpose. Furthermore, as atmospheric concentrations of CO₂ continue to increase in future years, it is the NBS intention to replace lower concentration SRM's of limited interest with new SRM's at higher concentrations to provide a standards set that will continue to bracket the atmospheric concentration range of interest.

One important operational aspect of NBS SRM's is worth noting. The sales of SRM's are managed under a self-perpetuating, non-profit recycling budget program to restock SRM's that are sold. Hence, once an SRM is in place, it does not require additional external funding to ensure its long-term availability, and it will continue to be available as long as the need for it exists. As long as there is an NBS, accurate and stable CO₂ in air SRM's will be available to serve the measurement calibration needs of the WMO atmospheric CO₂ global monitoring community.

The following portions of this position statement delineate: (I) the NBS response to the 1985 WMO recommendations developed at the meeting of experts at Lake Arrowhead, CA; and (II) plans for the long-term commitment of the NBS to the provision of accurate, stable U.S.
national standards (as SRM's) of CO₂ in air to support the immediate and long-range needs of the global monitoring community for atmospheric CO₂.

I. RESPONSE TO 1985 WMO RECOMMENDATIONS:

As a result of the November 1985 WMO international meeting of experts for global atmospheric CO₂ monitoring, the WMO expressed a need for NBS CO₂ in air SRM's and recommended that certain SRM's be prepared. The meeting attendees represented twelve countries: Australia, Canada, Federal Republic of Germany, France, Italy, New Zealand, Peoples Republic of China, Peru, South Korea, Spain, Switzerland, and the United States.

These recommendations were that the NBS: develop a CO₂ in air SRM at 360 ppm; ensure the availability of SRM's covering the range from 330-370 ppm CO₂ in air at about 10 ppm intervals; provide SRM's in cylinders larger than the standard 30 cu. ft. (0.84 m³) size (i.e., 150 cu. ft. size [4.2 m³]); and provide new SRM's in the future that stay ahead of the maximum atmospheric background levels as the atmospheric CO₂ concentrations increase.

In response to these recommendations, the NBS plans to:

- Develop an SRM having a CO₂ in air concentration in the vicinity of 360 ppm;
- In restocking SRM's 1670-72, provide three SRM's for the targeted suite of SRM's indicated in the table given below;
- Ensure that future CO₂ SRM's for global monitoring (including restocks of existing SRM's) will be available in air in aluminum cylinders having a capacity of 150 cu. ft. (4.2 m³);
- Provide future SRM's that continue to bracket the global atmospheric CO₂ concentration range of interest as the concentration of atmospheric CO₂ continues to increase.

Finally, in response to interests expressed at the 1985 WMO meeting, the NBS can provide, if deemed essential, at the cost of analysis, gravimetrically-based analyses of non-NBS CO₂ in air standards currently in use by intercomparisons to the NBS suite of primary gravimetric standards.

II. NBS PLAN

Based on the discussions and recommendations developed at the 1985 WMO meeting of experts, the NBS plans to have a recommended suite of SRM's in size 150 cu. ft. aluminum cylinders available for global monitoring. The current status and planned suite of these SRM's is summarized below:
### Carbon Dioxide in Air Concentration (ppm, by mole)

<table>
<thead>
<tr>
<th>Targeted Suite*</th>
<th>Currently Available</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>size 30 cu.ft.(^a)</td>
</tr>
<tr>
<td>340</td>
<td>SRM 2607</td>
</tr>
<tr>
<td>345</td>
<td>size 30 cu.ft.(^b)</td>
</tr>
<tr>
<td>350</td>
<td>size 30 cu.ft.(^c)</td>
</tr>
<tr>
<td>360</td>
<td>---d----</td>
</tr>
<tr>
<td>370</td>
<td>SRM 2609</td>
</tr>
</tbody>
</table>

*All in size 150 cu.ft. (4.2 m\(^3\)) aluminum cylinders.

\(^a\)SRM 1670, tentatively planned for restocking in size 150 cu.ft. at 330 ppm.

\(^b\)SRM 1671, tentatively planned for restocking in size 150 cu.ft. at 345 ppm.

\(^c\)SRM 1672, tentatively planned for restocking in size 150 cu.ft. at 350 ppm.

\(^d\)Planned for new highest priority SRM in size 150 cu.ft. at 360 ppm.

It should be noted from the above table that, with the exception of an SRM at 360 ppm, SRM's currently are available that bracket the nominal 330-370 ppm range of interest.

The restocking of SRM's 1670-72 will occur as the current stock of these SRM's is nearing depletion (approximately, December 1986, based on current inventories). Plans for the development of a new SRM at 360 ppm currently are in progress; it is anticipated that this new SRM will be made available by late 1986.

In the long term, in response to the anticipated continued increase in atmospheric CO\(_2\), the 330 ppm SRM may be replaced by a 380 ppm SRM and the 345 ppm SRM may be replaced by a 355 ppm SRM, to allow the targeted SRM suite to continue to be responsive to global monitoring needs.

### QUESTION DIRECTED TO THE WMO GLOBAL ATMOSPHERIC CO\(_2\) MEASUREMENT COMMUNITY CONCERNING THE USE OF NBS CO\(_2\) IN AIR SRM's

The NBS plan represents a long-term programmatic commitment to the provision of CO\(_2\) in air SRM's for global atmospheric monitoring. It is therefore important that information concerning the proposed suite of SRM's and the anticipated use of CO\(_2\) in air SRM's be obtained from the members of the WMO global measurement community to ensure that the near and longer term needs of the members of this community are fully satisfied.
SUMMARY:

It is the intention of the NBS to continue to provide CO$_2$ in air SRM's as long as the need exists. It also is the intention of the NBS to scientifically work with the WMO international community for atmospheric CO$_2$ measurements to ensure that stable, accurate standards needs are adequately addressed.
ANNEX III

LIST OF PARTICIPANTS

1. Hee Seung Choi
   Korean Meteorological Service
   l-Song Wul Dong, Chong Ko-Ku
   Seoul 110, Republic of Korea  (02) 723-0011 or 0017

2. Luigi Ciattaglia
   Servizio Meteorologico dell'Aeronautica
   Observatorio Vigna di Valle
   I-00062 Bracciano - Roma, Italy  6 + 9023953

3. Thomas J. Conway
   NOAA/ARL/GMCC RE/RE/AE4
   325 Broadway
   Boulder, Co 80303, U.S.A.  (303) 497-6681

4. Pedro De Pablo Ricote
   Observatorio Meteorologico de Izaña
   38071 Santa Cruz de Tenerife, España  (922) 332303

5. William P. Elliott
   Air Resources Lab. NOAA R/AR
   8060 13th Street
   Silver Spring, Md 20910, U.S.A. (301) 427-7684

6. André Gaudry
   Centre des Faibles Radioactivités
   Laboratoire Mixte CNRS/CEA
   Avenue de la Terrasse
   P-91190 Gif sur Yvette, France (6907) 7828 ext. 788

7. Rolf Graul
   Umweltbundesamt - Station Schauinsland
   Postfach 1229
   D-7815 Kirchzarten, Federal Republic of Germany  (07602) 265

8. Peter Guenther
   Scripps Institution of Oceanography
   University of California, San Diego
   La Jolla, Ca 92093, U.S.A.  (619) 452-4230

9. Ernest E. Hughes
   National Bureau of Standards - Gas Metrology Group
   Chemistry Building, Room B364
   Gaithersburgh, Md 20899, U.S.A. (301) 921-2888

10. Mutsumi Ishitsuka
    Instituto Geofisico del Peru
    Observatorios de Huancayo y Cosmos
    Huancayo, Peru  (23) 4401
ANNEX III, p. 2

11. Ramon Juega Buide
    Observatorio Meteorologico de Izaña
    38071 Santa Cruz de Tenerife, Espana
    (922) 332303

12. Charles D. Keeling
    Scripps Institution of Oceanography
    University of California, San Diego
    La Jolla, Ca 92093, U.S.A.
    (619) 452-4230

13. Ingeborg Levin
    Institut fur Umweltphysik, Universitaet Heidelberg
    Im Neuenheimer Feld 366
    D-6900 Heidelberg, Federal Republic of Germany
    (06221) 563330
    telex: 461745 UNIKL D

14. Martin Manning
    Institute of Nuclear Sciences
    Dept. of Scientific and Industrial Research
    Private Bag
    Lower Hutt, New Zealand
    (04) 666-919

15. David Moss
    Scripps Institution of Oceanography
    University of California, San Diego
    La Jolla, Ca 92093, U.S.A.
    (619) 452-4230/2780

16. Graeme Pearman
    CSIRO Division of Atmospheric Research
    Private Bag No. 1
    Mordialloc, 3195 Victoria, Australia
    telex: ASPEN AA34463
    (03) 580-6333
    FAX (03) 580 6933

17. James T. Peterson
    U.S. Dept. of Commerce/NOAA
    325 Broadway
    Boulder, Co 80303, U.S.A.
    (303) 497-6650

18. Peter Pohl
    Institute of Nuclear Sciences
    Dept. of Scientific and Industrial Research
    Private Bag
    Lower Hutt, New Zealand
    (04) 666-919

19. Pedro Sancho Diaz
    Dpto. de Fisica, Universidad de la Laguna
    La Laguna, Tenerife, Espana
    (922) 258234

20. Pieter Tans
    NOAA/GMCC R/E/AR4
    325 Broadway
    Boulder, Co 80303, U.S.A.
    (303) 497-6678

21. Neil B.A. Trivett
    Atmospheric Environment Service
    4905 Dufferin Street
    Downsview, Ontario M3H 5T4, Canada
    (416) 667-4954
22. C.S. Wong  
Marine Carbon Research Centre, Institute of Ocean Sciences  
P.O. Box 6000  
9860 west Saanish Road  
Sidney, B.C. V8L 4B2, Canada (604) 656-8407

23. Yupu Wen  
State Meteorological Administration  
Atmospheric Chemistry Laboratory  
46 Baishiqiolu  
Beijing, China (89) 0371-2646

24. Walter Zielinsky  
National Bureau of Standards – Gas Metrology Group  
Chemistry Building, Room B364  
Gaithersburgh, Md 20899, U.S.A. (301) 921-2886/921-2888

WMO Secretariat:

Albert Köhler  
World Meteorological Organization  
Environment Division  
case postale no.5  
CH-2111 Genève 20, Suisse (022) 346400 ext. 455  
telex: 23260A OMM CH
ANNEX IVA

BRIEF REPORT ON THE AUSTRALIAN (CSIRO) CARBON DIOXIDE MONITORING PROGRAM

G.I. PEARMAN

Introduction

The CSIRO Division of Atmospheric Research has maintained an atmospheric carbon dioxide ($CO_2$) monitoring program since 1972. The purpose of the program has been to provide information concerning the time and space variability of $CO_2$ concentration which can be used to further understanding of the global carbon cycle. The importance of data in the southern hemisphere has been accepted as a special responsibility of the program.

The program has consisted of two parts, discrete sampling of air collected from aircraft and analysed at the Central Laboratory at Aspendale (Melbourne) and surface observations, both via flask sampling and in situ analysis at several locations in Australia and Antarctica. The most comprehensive surface observatory is maintained at the Australian Baseline Observatory as part of the Australian commitment to the BAPMO Network.

Distribution of Sampling Sites

Figure 1 shows the flight paths over which flasks samples have been collected, in most cases for 10 years or more.

Figure 2 shows the distribution of surface observatories including the continuous station at Cape Grim and the quasi-continuous station at Macquarie Island.

Techniques and Results

It is not necessary here to describe the details of how the CSIRO program is operated. Technical details of the aircraft measurement program including discussions of calibration and carrier gas correction are fully described in Beardsmore et al. (1978) and Pearman
et al. (1983). These technical reports are readily available from
CSIRO.

Similar technical details of the surface station program are
given in Beardsmore et al. (1984).

Descriptive presentations of the data for the program are
given in Pearman and Beardsmore (1984), and Beardsmore and Pearman
(1985). These papers refer to a number of other papers in which the
Australian data, together with those from other national programs, has
been used in studies of the global carbon cycle.

Archiving of whole air samples in high pressure tanks was
commenced in 1978. Initially only 2-3 tanks were archived each year.
At present this number has been increased to 12.

Carbon Isotopes

The cryogenic extraction of CO$_2$ from air at the Cape Grim
Observatory, for the purpose of stable isotope analyses, commenced in
1977 (Baseline, 1981; Baseline, 1983). The early results were
summarized by Goodman (1980).

At the end of 1981, the extraction equipment was modified and
relocated, resulting in a marked improvement in precision (Francey,
1985a). Preliminary results for the period 1982-1984 exhibit a secular
trend of 0.025 ± 0.005 0/oo yr$^{-1}$ and a seasonal variation of p-p
amplitude of 0.055 ± 0.014 0/oo with a maximum on day 85 ± 15 (26 March)
(Francey, 1985b).

A detailed discussion of the systematic influences on, and
selection criteria of, the Cape Grim isotope data will appear in
Baseline (1986).

Supplementing these results, a program of monthly air sample
collections from Alaska, Hawaii, Samoa, Cape Grim and South Pole
commenced in 1984, in co-operation with NOAA/GMCC. These flasks are
providing information on the latitudinal distribution of $^{13}$C/$^{12}$C.
Extension of sampling to Mawson, Macquarie Island and the upper
troposphere over south eastern Australia has commenced.
Both of these programs utilize dry air so that information on the spatial and secular variations in the $^{18}O/^{16}O$ ratio of CO$_2$ is obtained. The Cape Grim data are discussed by Tans, Francey and Pearman (Baseline, 1986).

A small co-operative program with the Australian National University has yielded $^{14}C$ determinations at monthly intervals in Cape Grim air since 1982 (Baseline, 1986). Since 1984 CO$_2$ samples from the cryogenic extraction apparatus have been archived for possible accelerator mass spectrometer $^{14}C$ analysis.
ANNEX IVA, p. 4

References


Goodman, H.S., (1980), The $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric carbon dioxide at the Australian baseline station, Cape Grim. pp.111-114 of In Carbon Dioxide and Climate: Australian Research (Ed. G.I. Pearman), Australian Academy of Science, Canberra, 217 pp.


Figure Captions

Figure 1: The CSIRO aircraft air-sampling network showing details of flight paths, aircraft and cooperating agencies.

Figure 2: A map of the location of the observatory sites used in the CSIRO surface monitoring program for atmospheric carbon dioxide.
ATMOSPHERIC CO₂ MEASURING PROGRAM IN CANADA

(Organization: Ocean Sciences and Surveys
Department of Fisheries and Oceans)

The Marine Carbon Research Centre at the Institute of Ocean Sciences, Sidney, B.C. has been acting as the analytical laboratory of atmospheric CO₂ contents in air samples collected under both the BAPMoN sites by the Atmospheric Environment Service of Canada and the Oceanic CO₂ program by Ocean Sciences of Surveys. The programs conducted by MCRC on marine atmospheric CO₂ are: (1) Cape St. James Lighthouse on Queen Charlotte Islands: 2L air flask samples for CO₂, (2) Ship-of-opportunity on M.V. Lillooet between Vancouver, B.C. and Brisbane, Australia: (a) 2L air flask samples for CO₂, (b) 5L air flask samples for $^{13}$C/$^{12}$C, (3) Continuous measurements of atmospheric CO₂ and oceanic pCO₂ on board the M.V. Lillooet by gas chromatograph and (4) Continuous measurements of atmospheric and oceanic pCO₂ by infrared on Line P between Sidney, B.C. and Ocean Station P ($50^\circ$N $145^\circ$W).
Report of the CFR Laboratory (France) on Calibrating Experiences

Since 1981, the CFR has used gravimetric CO₂ standards accurately produced by the L'Air Liquide Company.

In a first step, the standard gases were prepared in N₂. However, because of the carrier gas effect of the NDIR analyzers, and its possible evolution during the aging of the device, it has been found preferable to develop and use standard gases in synthetic air.

We describe below the behaviour of this last kind of standards:

A. Production:

1. CO₂ is weighed in a small cylinder (C1)
   - weight of CO₂ = about 4.8 g
   - weight of the cylinder C1 = 140 g
   - capacity of the balance = 160 g
   - accuracy of the balance = 0.1 mg

2. A previous mixing of oxygen and argon (for CO₂-in-air) is gravimetrically produced in a big 50 liter-cylinder (C3)

3. CO₂ is transferred into a 50 liter-cylinder (C2), then rinsed 5 times by the O₂ and argon mixing

4. Oxygen and argon is weighed in C2
   - weight of C2 = 70 kg
   - capacity of the second balance = 100 kg
   - accuracy of the balance = ± 0.1 g

5. The cylinder C2 is completed with N₂

6. The concentrations are converted in mole fraction in air from the different accurate weighings.

B. Purity of the gases of the mixing:

All gases used are highly pure gases, better than 99.998% for CO₂ and O₂ and still better (99.9999%) for N₂ and Argon. The purity criteria are described in the Table 1.
### Table 1

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>N₂</th>
<th>O₂</th>
<th>Ar</th>
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<tbody>
<tr>
<td>Z</td>
<td>99.998</td>
<td>99.9999</td>
<td>99.998</td>
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<table>
<thead>
<tr>
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<th>(ppm)</th>
<th>(ppm)</th>
<th>(ppm)</th>
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<td>&lt;1</td>
<td>&lt;3</td>
<td>&lt;1</td>
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<td>&lt;0.2</td>
<td>&lt;0.1</td>
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<tr>
<td>CO₂</td>
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<td>&lt;0.2</td>
<td>&lt;0.1</td>
</tr>
<tr>
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<td>&lt;0.1</td>
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<td>&lt;0.1</td>
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<td>Ar</td>
<td>&lt;3</td>
<td>&lt;12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### C. Final Content and Accuracy

The synthetic air is determined with a high accuracy for O₂ and Argon as following:

1. **Primary standards** (gravimetric gases)
   
   \[
   O_2 = 20.9 \pm 0.2\% \\
   Ar = 0.93 \pm 0.03\% \\
   N_2 = 78.17\%
   \]

   Up to date the CO₂ concentrations in such mixings were produced according to the CFR requirements. In the future, the approximate concentrations will be proposed (ppm, mole fraction): 330, 335, 340, 345, 350, 355, (360). The accuracy attained is 0.25 ppm (0.15 ppm for standard gases in N₂).

2. **Working gases** (manometric gases, less accurate)
   
   O₂, Ar, and N₂ have the same concentration as for primary standards.
The concentrations proposed (ppm, mole fraction) are 330, 355, with an accuracy of ± 3 ppm.

3. An analytical control is performed by means of an ADC non-dispersive infrared analyser, and by comparison to other accurate gases kept at the Company.

D. Comparison with the 1984 provisional SIO scale:

Table 2 gives the whole results.

The 4 first cylinders have been directly certified by SIO, and expressed in the provisional 1984 SIO Scale (Column SIO (1)). The result of the intercomparability appears in column AL-SIO 1. If the results are converted to the 1985 SIO scale this intercomparability is still better (see Table 3).

A second set of comparisons have been performed at the CFR by comparing other accurate standards of the L'Air Liquide with respect to the 4 concentrations directly certified. This comparison has been achieved for 10 B5 - cylinders. Results of this first comparison appear in Column SIO 1, the difference between SIO 1 and AL in column Al - SIO 1. The results agree (by taking the 1984 scale) within 0.2 to 0.3 ppm. After conversion to the 1985 SIO Scale, the intercomparability do not exceed 0.18 ppm (see Table 3) which confirms the accuracy given by L'Air Liquide.

A second secondary comparison has been performed one year and half after the first one. Results are given in column SIO (2), the difference between AL and SIO (2) in column Al - SIO 2. The column SIO 1 - SIO 2 gives an idea of the drift of the concentration with the small B5 cylinders in aluminum. The expected drift of the 50 l stainless steel cylinders should be much lower, the pressure remaining high a longer time.
Table 2

<table>
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<tr>
<th>REF</th>
<th>AL</th>
<th>SiO(1)</th>
<th>SiO(2)</th>
<th>AL-SiO1</th>
<th>AL-SiO2</th>
<th>SiO1-SiO2</th>
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</thead>
<tbody>
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<td>B50</td>
<td>3166017</td>
<td>332.86</td>
<td>332.49</td>
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<td>B50</td>
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<td></td>
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<td></td>
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<tr>
<td>B50</td>
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<td></td>
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<tr>
<td>B5</td>
<td>3184184</td>
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<td>331.80</td>
<td>331.67</td>
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<td>B5</td>
<td>3184182</td>
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<td>B5</td>
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<td>336.63</td>
<td>0.31</td>
<td>0.37</td>
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<tr>
<td>B5</td>
<td>3184114</td>
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<tr>
<td>* B5</td>
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<td>339.55</td>
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<tr>
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<td>345.15</td>
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<td>0.02</td>
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<td>** B5</td>
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<td></td>
<td></td>
<td>0.17</td>
</tr>
<tr>
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<td>329.33</td>
<td></td>
<td></td>
<td>0.22</td>
</tr>
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<td>0.30</td>
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<td>**** B10 N.B.S.</td>
<td>342.3</td>
<td>342.51</td>
<td></td>
<td></td>
<td></td>
<td>-0.21</td>
</tr>
</tbody>
</table>

Notes:

* this cylinder was loaded with 10 ppm of CH₄

** this cylinder was loaded with 9.7 ppm of CO

*** this cylinder was loaded with 10 ppm of N₂O

**** the value in column AL is the nominal concentration given by NES
Table 2 - Intercomparison between the SIO certified concentrations and the nominal concentrations proposed by L'Air Liquide B50, B5, B10 respectively referred to cylinders of capacities of 50 liters (stainless steel), 5 liters (aluminum) and approximately 10 liters (provided by the NBS);

- REF is the number of the cylinder;
- AL is the nominal concentration provided by L'Air Liquide;
- SIO (1) is the direct determination of 4 cylinders (B50) N6 3166017, 3165962, 3166119, 326103, by SIO. The values in the same column referring to B5 cylinders are secondary determination with respect to the 4 preceding ones, the whole of them being in the provisional 1984 SIO scale;
- SIO (2) is a second secondary determination achieved one year and a half after the first one;
- AL-SIO (1) is the difference between the corresponding figures in the two columns AL and SIO (1);
- AL-SIO (2) is the difference between the corresponding figures in the column AL and SIO (2);
- SIO (1) - SIO (2) is the difference between the corresponding figures in the column SIO (1) - SIO (2), which represent an eventual evolution of the concentration in the small aluminum cylinders.
E. Commercial Availability:

Only 50 liter cylinders in stainless steel could be delivered with a 150 to 160 bars pressure. The L'Air Liquide CO$_2$ standards could be available through foreign depositories which are listed below:

TABLE 3

By changing the provisional 1984 SIO scale like the 1985 SIO scale which is preferable to use, the differences between AL and SIO(1) become as follows:

<table>
<thead>
<tr>
<th>AL - SIO(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
</tr>
<tr>
<td>B50 3166017</td>
</tr>
<tr>
<td>B50 3165962</td>
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<tr>
<td>B50 3166119</td>
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<tr>
<td>B5  3184108</td>
</tr>
<tr>
<td>B5  3184177</td>
</tr>
</tbody>
</table>
NOAA/GMCC CO₂ Measurement Program

1. Gas Standards and Calibration Techniques

The NOAA/GMCC standards and calibration techniques for CO₂ measurements have been described in detail by Komhyr et al. (1985a), so only a brief description will be given here. A suite of secondary standards ranging in concentration from about 300 to 400 ppm is maintained in Boulder and a subset of these is calibrated at the CCL approximately every two years. The secondary standards are used to calibrate a set of tertiary standards at least once per year. All station standards, station working gases, and flask analysis working gases are calibrated against the tertiary standards.

At the continuous analyzer field sites at Barrow, Mauna Loa, Samoa and South Pole, 4 station standards are analyzed once per week to determine the analyzer response curve and to monitor the working gases for drift. When the pressure in a station standard gas cylinder reaches 500 psi a final calibration is performed and the cylinder is refilled.

Calibrations have been performed using UNOR 2, URAS 2T and Siemens ULTRAMAT III analyzers. Calibration values are determined from a quadratic fit to 4 standards. Each gas being calibrated is analyzed 10 times resulting in a typical measurement precision (1σ) of 0.02 to 0.08 ppm. All gases are passed through a glass cryo trap maintained at -70°C.
2. Field Measurements and Analytical Techniques

A. Continuous analyzer program

Continuous atmospheric CO₂ concentration measurements are made at Barrow, Samoa and South Pole with URAS 2T analyzers. An URAS 2 analyzer is used at Mauna Loa. The ambient air is sampled from an intake system by means of a diaphragm (Viton) pump. The ambient air and the reference gases flow through a glass cryo trap at -70°C and then through the analyzer cell at a rate of 300 cc min⁻¹. The ambient air is sampled for 50 minutes followed by 5 minutes each of two reference gases chosen to bracket the ambient concentration with a span of ~10 ppm. After each gas switch there is a delay to allow the analyzer signal to stabilize before the analog signal is converted to digital values which are stored on tape (see Section , this report).

The data tapes and stripchart records are returned to the Boulder laboratory for processing to CO₂ concentration values. The first stage of data scrutiny consists of removing instrumentally defective data from the record and filling in gaps in the digitally recorded data by hand reducing the stripchart record when possible. Also at this stage the stripcharts are inspected visually and periods of high within-hour variability are flagged.

B. Flask sampling program

The sampling and analytical procedures employed in the NOAA/GMCC flask sampling program and an analysis of the 1968-82 data are given in Komhyr et al. (1985b). Presently, whole air flask samples are collected in 0.5 l glass, greased stopcock flasks at 25 cooperative sites, using a portable flushing and pressurizing pump. Samples are returned to the Boulder laboratory for
analysis with a typical storage time between collection and analysis of ~2 weeks, with the exception of samples from remote sites in the southern hemisphere where storage times range from several months to more than one year.

The flask samples are analyzed in Boulder on a semiautomatic flask analysis apparatus (Komhyr, et al. 1983). The samples and reference gases are dried in the same cryo trap at -70°C before analysis. The flask analyzer response curve is determined weekly using three reference gases. Several methods are used to ensure flask sample data quality. Flasks filled in the lab with gases of known concentration are analyzed on every analysis day to monitor analyzer performance. At several sampling sites GMCC samples are collected quasi-simultaneously with samples of other measurement programs (SIO, CSIRO, etc.). The results for these samples are compared to evaluate sampling and measurement methodologies. In addition, at the four GMCC baseline observatories, samples are collected in a variety of flask types by different methods to further evaluate methodologies.

3. Reporting and Publication of Data

NOAA/GMCC continuous analyzer provisional daily means are reported to WMO and are archived with the National Climatic Data Center at Asheville, N.C. Reports detailing the operation and the data through 1982 for each baseline observatory are currently in preparation.

The GMCC flask data from 1968-1982 are archived in the 1983 WMO scale with the Carbon Dioxide Information Center at the Oak Ridge National Laboratory, Knoxville, Tennessee. An analysis of these data is given by Komhyr et al., 1985b. The 1983 and subsequent flask data will be submitted to WMO for inclusion in provisional data reports.
REFERENCES:


Figure caption:

Annual mean CO₂ concentration vs. sin(latitude) for measurements made at background sites by seven of the organizations represented at the 1985 WHO Meeting of Experts (CSIRO, Australia; AES and IOS, Canada; CFR, France; Tohoku University, Japan; Institute of Nuclear Sciences, New Zealand; and NOAA and SIO, USA). Much of the data shown here is as yet unpublished and was made available to the meeting participants for the purpose of intercomparison. Also, these annual means are provisional pending adjustments to standard calibration values and final data selection, which will probably affect the 1984 data more than the earlier years. The records at some sites contain gaps and no attempt has been made to correct for any biasing of the annual means due to the lack of a portion of the seasonal cycle. The curves are hand-drawn and are intended as visual aids in comparing the data.
### Daily atmospheric carbon dioxide mean values for 1984

*DATA ARE CORRECTED FOR CARRIER GAS EFFECT and given in ppm above 300 (adjusted to the 1985 Mole Fraction Scale) - prepared in October 1985 -*

| DAY | JAN | FEB | MAR | APR | MAY | JUN | JUL | AUG | SEP | OCT | NOV | DEC |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   | 41.75 | 41.50 | 41.97 | - | 42.44 | 42.95 | - | 42.39 | - | - | - | - |
| 2   | 41.63 | - | - | - | - | - | - | - | - | - | - | - |
| 3   | 42.05 | 41.96 | - | - | - | - | - | - | - | - | - | - |
| 4   | 41.98 | 41.67 | 41.81 | 41.83 | - | - | - | - | - | - | - | - |
| 5   | 41.58 | 41.90 | - | - | - | - | - | - | - | - | - | - |
| 6   | 41.99 | 41.35 | - | - | - | - | - | - | - | - | - | - |
| 7   | - | 41.33 | 43.05 | - | - | - | - | - | - | - | - | - |
| 8   | 41.94 | 42.72 | 42.18 | - | - | - | - | - | - | - | - | - |
| 9   | 41.91 | 42.37 | - | - | - | - | - | - | - | - | - | - |
| 10  | 41.67 | 41.64 | - | - | - | - | - | - | - | - | - | - |
| 11  | 41.83 | 41.57 | - | - | - | - | - | - | - | - | - | - |
| 12  | 41.77 | 43.39 | 42.93 | - | - | - | - | - | - | - | - | - |
| 13  | - | 42.77 | 43.12 | - | - | - | - | - | - | - | - | - |
| 14  | 41.74 | 42.60 | 42.77 | - | - | - | - | - | - | - | - | - |
| 15  | 41.69 | 41.67 | - | - | - | - | - | - | - | - | - | - |
| 16  | 41.53 | 41.97 | - | - | - | - | - | - | - | - | - | 42.71 |
| 17  | 41.75 | 41.56 | - | - | - | - | - | - | - | - | - | - |
| 18  | 41.70 | 41.28 | - | - | - | - | - | - | - | - | - | - |
| 19  | - | 43.40 | 43.17 | 42.88 | 42.71 | - | - | - | - | - | - | - |
| 20  | 41.50 | 42.40 | 42.9 | - | - | - | - | - | - | - | - | - |
| 21  | 41.85 | 42.09 | 42.09 | - | - | - | - | - | - | - | - | - |
| 22  | - | 43.04 | 43.17 | - | - | - | - | - | - | - | - | - |
| 23  | 42.19 | - | - | - | - | - | - | - | - | - | - | - |
| 24  | 42.03 | 41.79 | 41.24 | - | - | - | - | - | - | - | - | - |
| 25  | - | 42.79 | - | - | - | - | - | - | - | - | - | - |
| 26  | 41.72 | - | - | - | - | - | - | - | - | - | - | - |
| 27  | 42.32 | - | - | - | - | - | - | - | - | - | - | - |
| 28  | 41.96 | 41.55 | - | - | - | - | - | - | - | - | - | - |
| 29  | 41.74 | 41.65 | 41.43 | - | - | - | - | - | - | - | - | - |
| 30  | - | - | - | - | - | - | - | - | - | - | - | - |
| 31  | - | 42.61 | 42.77 | 42.66 | - | - | - | - | - | - | - | - |

**MONTH** | **341.94** | **341.73** | **341.68** | **341.63** | **341.89** | **342.53** | **343.04** | **343.07** | **342.81** | **342.58** | **343.09** | **342.36**
---|---|---|---|---|---|---|---|---|---|---|---|---|
**REL.C** | **99.88** | **99.81** | **99.80** | **99.79** | **99.86** | **100.05** | **100.20** | **100.21** | **100.13** | **100.06** | **100.21** | **100.00**
**STDEV** | **0.24** | **0.23** | **0.26** | **0.16** | **0.54** | **0.39** | **0.34** | **0.25** | **0.28** | **0.54** | **0.32** | -
**NHRS** | **119** | **0** | **94** | **75** | **82** | **56** | **53** | **91** | **195** | **81** | **141** | **13**
**N COV** | **16** | **0** | **13** | **10** | **11** | **8** | **7** | **12** | **27** | **11** | **20** | **2**

**ANNUAL AVERAGE: 342.35**

**NOTE: THE HUNDREDTH DIGIT OF THE ABOVE CARBON DIOXIDE CONCENTRATIONS MAY NOT HAVE SIGNIFICANCE !**
Daily atmospheric carbon dioxide mean values for 1984

PROVISIONAL DATA above 300 ppmv (SIO I83 scale)
(Flask sampling programme)

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<th>APR</th>
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**MONTH** 343.6 343.6 342.8 344.6 344.4 343.8 343.8 343.4 343.74

**REL.C** 100.0 99.9 99.7 100.3 100.2 100.0 100.0 99.9 100.0

**STDEV** 1.6 2.5 0.7 1.3 1.4 1.2 1.5 1.9 1.5

**N (F)** 9 3 0 0 0 4 15 15 10 8 0 7 6

**W (F) = number of flasks selected**

* = rejected (bad) pair  & = not representative of background conditions and rejected
$ = rejected due to experimental deficiency

**ANNUAL AVERAGE:** 343.98

MAHE ISLAND
(Seychelles)

WMO BAPMoN station:
(NOAA/GMCC programme)
A cryogenic collecting sampler for the collection of trace amounts of gases and vapors from air is shown in Figure 1. The design and description of the sampler was first reported by M. Shephard (in Proceedings of the United States Technical Conference on Air Pollution, Louis C. McCabe, Ed., McGraw-Hill, New York, 1952, pp. 228-230). The centre cap at the top of the sampler was added as a safety modification in the event of pressure buildup in the sampler. The sampler is constructed of glass and is immersed in a bath of a suitable cryogen, depending on the gases or vapors one is interested in removing from the inlet air stream. The air stream is drawn through the sampler by a pump attached to the outlet end of the sampler. The air stream enters the sampler and sequentially passes through the inner tube, through the snug glass wool ring filter mat separating the inner tube from the outer tube, and leaves the sampler through the outlet. The filter serves to entrain aerosol fog or particulate produced by the vapors and gases being condensed. The sampler has been used to effectively remove water vapor and other air components.


7. Fourth Analysis on Reference Precipitation Samples by the Participating World Meteorological Organization Laboratories by Robert L. Lampe and John C. Puzak, December 1981*

8. Review of the Chemical Composition of Precipitation as Measured by the WMO BAPMoN by Prof. Dr. Hans-Walter Georgii, February 1982


11. Summary Report on the Status of the WMO Background Air Pollution Monitoring Network as at May 1982*

12. Report on the Mount Kenya Baseline Station Feasibility Study edited by Dr. Russell C. Schnell


14. Effects of Sulphur Compounds and Other Pollutants on Visibility by Dr. R.F. Pueschel, April 1983

15. Provisional Daily Atmospheric Carbon Dioxide Concentrations as Measured at BAPMoN Sites for the Year 1981, May 1983*

* Out of stock

(RDP 2566)

17. General Consideration and Examples of Data Evaluation and Quality Assurance Procedures Applicable to BAPMoN Precipitation Chemistry Observations by Dr. Charles Hakkari, July 1983


19. Forecasting of Air Pollution with Emphasis on Research in the USSR by M.E. Berlyand, August 1983

20. Extended Abstracts of Papers to be Presented at the WMO Technical Conference on Observation and Measurement of Atmospheric Contaminants (TECOMAC), Vienna, 17-21 October 1983


23. Provisional Daily Atmospheric Carbon Dioxide Concentrations as Measured at BAPMoN Sites for the Year 1982. November 1984


26. Sulphur and Nitrogen in Precipitation: An Attempt to Use BAPMoN and Other Data to Show Regional and Global Distribution by Dr. C.C. Wallén. April 1986


28. Report on the Meeting of Experts on the East Atlantic and Mediterranean Transport Experiment (EAMTEX) (Madrid, Spain 6-7; Salamanca, Spain, 8 November 1984) (in preparation)

29. Recommendations on Sunphotometer Measurements in BAPMoN Based on the Experience of a Dust Transport Study in Africa by Dr. Guillaume A. d'Almeida. September 1985


33. Man and the Composition of the Atmosphere: BAPMoN - An international programme of national needs, responsibility and benefits by R.F. Pueschel (in preparation)


35. Provisional Daily Atmospheric CO₂ Concentrations as Measured at BAPMoN Sites for the Year 1983. December 1985


