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ISOTOPIC CARBON ANALYSIS OF METEORITIC
ORGANIC MATTER

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SUMMARY

The purpose of this research was to determine the carbon isotopic ratios of the carbonaceous matter present in meteorites and related terrestrial materials, and to construct the necessary mass spectrometric apparatus to effect these measurements. Emphasis was placed on the carbon isotopic composition of carbonaceous chrondrites, graphite nodules of iron meteorites, and some organic geochemical samples of presumed igneous or geothermal origin. The need for this work was based on the relative scarcity of isotopic measurements on terrestrial and extraterrestrial samples, and the inconsistency of those which were available. It was also considered that measurements on particular chemical fractions of the samples may demonstrate errors in the early work and provide more meaningful information.

Although the principal experimental objective was the obtention of relevant isotopic data, the most time consuming aspect was the design, construction, and testing of the necessary apparatus and instrumentation. The design objective to build an instrument that could measure isotope ratio differences for carbon to within $\pm.05$ parts per mil was accomplished. To meet this goal in a limited time schedule, design construction and testing phases were run concurrently. The pretreatment apparatus, sample preparation, sample introduction, mass spectrometric instrumentation, and data handling equipment were built while the sample acquisition, fractionation, and analytical chemical composition were performed. The latter was done by means of an LKB 9000 gas chromatograph-mass spectrometer. The specific isotopic analytical objectives included careful selection of samples, separation of any carbonaceous material into some major fractions, and quantitative conversion of these fractions into carbon dioxide from which the C^{13} and C^{12} isotopes could be measured.

With this new instrument, the following findings were made: (1) The C^{13}/C^{12} ratio of several graphite-troilite nodules of iron meteorites gave an average value of -7 per mil which, interestingly enough, coincides with the value for terrestrial igneous carbon (diamond or carbonatites) of presumed primordial origin. (2) After appropriate treatment with acids, values of approximately +60 per mil for the carbonate of the Orgueil meteorite and -12 to -30 per mil for the reduced carbon of various carbonaceous chondrites were obtained. Therefore, the carbonate of Orgueil could not have been in equilibrium with any biota on the meteorite parent body. (3) The inconsistent results obtained previously by other authors on the C^{13}/C^{12} ratio of carbonaceous chondrites were probably the result of the admixture in different proportions of the above two carbon phases: oxidized (carbonate) and reduced carbon. (4) Values obtained for some organic geothermal inclusions which had been fractionated into paraffinic, aromatic, and polar fractions, gave typical values corresponding to material of biological origin. Therefore, their presumed igneous origin is probably incorrect. On the basis of these results any future work on carbon isotopes of carbonaceous chondrites, or, for that matter, an any samples, should be preceded by a careful separation into at least the above major phases if the results must have a meaningful interpretation.

INTRODUCTION

Many investigations have been carried out in recent years to determine the nature and amount of organic matter present in meteorites, especially those classified as carbonaceous chondrites. The investigators working in this area have been led to widely varying conclusions in interpreting their experimental results. An especially relevant question which has not been solved is which of the organic components identified in meteorites are terrestrial contamination, and alternatively, what part of the organic matter is indigeneous. The extensive investigations carried out in recent years to study carbon isotope fractionation in terrestrial materials have established that the C^{13}/C^{12} isotope ratio falls within a well defined and rather narrow range for all terrestrial carbon bearing materials. A measurement of the stable carbon isotope ratio of the organic components may then provide the additional evidence necessary to distinguish meteorite indigeneous organic matter from terrestrial contamination.

The investigations by Boato (1) have shown that certain significant stable carbon isotope variations do exist in meteoritic organic material. He has measured C^{13}/C^{12} ratios from chondrites with the following results.

Meteorite Classification	δC^{13} parts per mil
Carbonaceous chondrites	-3.7 to -11.4
Olivine-pigeonite chondrites	-12.9 to -18.8
Olivine-bronzite chondrites	-24
One enstatite chondrite (Indarch)	(-) 12.9

These values show a consistent sequence from carbonaceous chondrites through olivine-pigeonite chondrites to olivine-bronzite chondrites with the enstatite chondrite showing a close relationship to carbonaceous chondrites. Boato states this could "possibly represent a preferential loss of C^{13} during the process in which the volatiles were lost from the original material from which the various groups of carbon were formed. Type I carbonaceous chondrites are probably closest in bulk

composition to this original material. On the other hand, accumulation in isotopically different carbon compounds can not be ruled out as an explanation." It is obvious that analyses of individual fractions of meteoritic material would yield additional information on the nature and genesis of the material.

In a recent paper, Hayes (2) has reviewed recent data on isotope ratio studies, some of which are in agreement with Boato's but some of which are in disagreement, "so that the situation is, at the moment, unclear." It would appear that the tentative conclusions reached, namely: (a) that some forms of meteoritic carbon have isotope ratios which lie outside terrestrial ranges and (b) that the carbon in carbonaceous chondrites may be richer in C^{13} than in ordinary chondrites, need further testing, to say the least.

The measurement of the C^{13}/C^{12} ratios in the insoluble and different extractable fractions of meteoritic organic matter and related terrestrial materials has therefore been carried out in this study. This method has received little attention by those studying meteoritic organic matter even though it offers considerable promise in identifying terrestrial contaminants, and perhaps even more important may provide data on the mechanism by which these compounds were formed.

In order to obtain C^{13} isotopic data with the necessary accuracy required to be able to arrive at meaningful conclusions concerning the source and mechanism of formation of meteoritic organic matter, a precise isotope ratio measurement system was designed, constructed, and evaluated to determine its capabilities. The design objective was to construct a system capable of measuring carbon isotope ratio differences with a precision of $\pm$ 0.005 percent. Some articles (3-6) have been published recently describing various aspects of isotope ratio instrumentation, but no complete and comprehensive description of a high precision measurement system has been presented in recent years. A detailed description sufficient to allow one to fabricate, assemble and operate a complete isotope ratio measurement system is given. The system described here incorporates the most modern electronics available; and it is simpler to
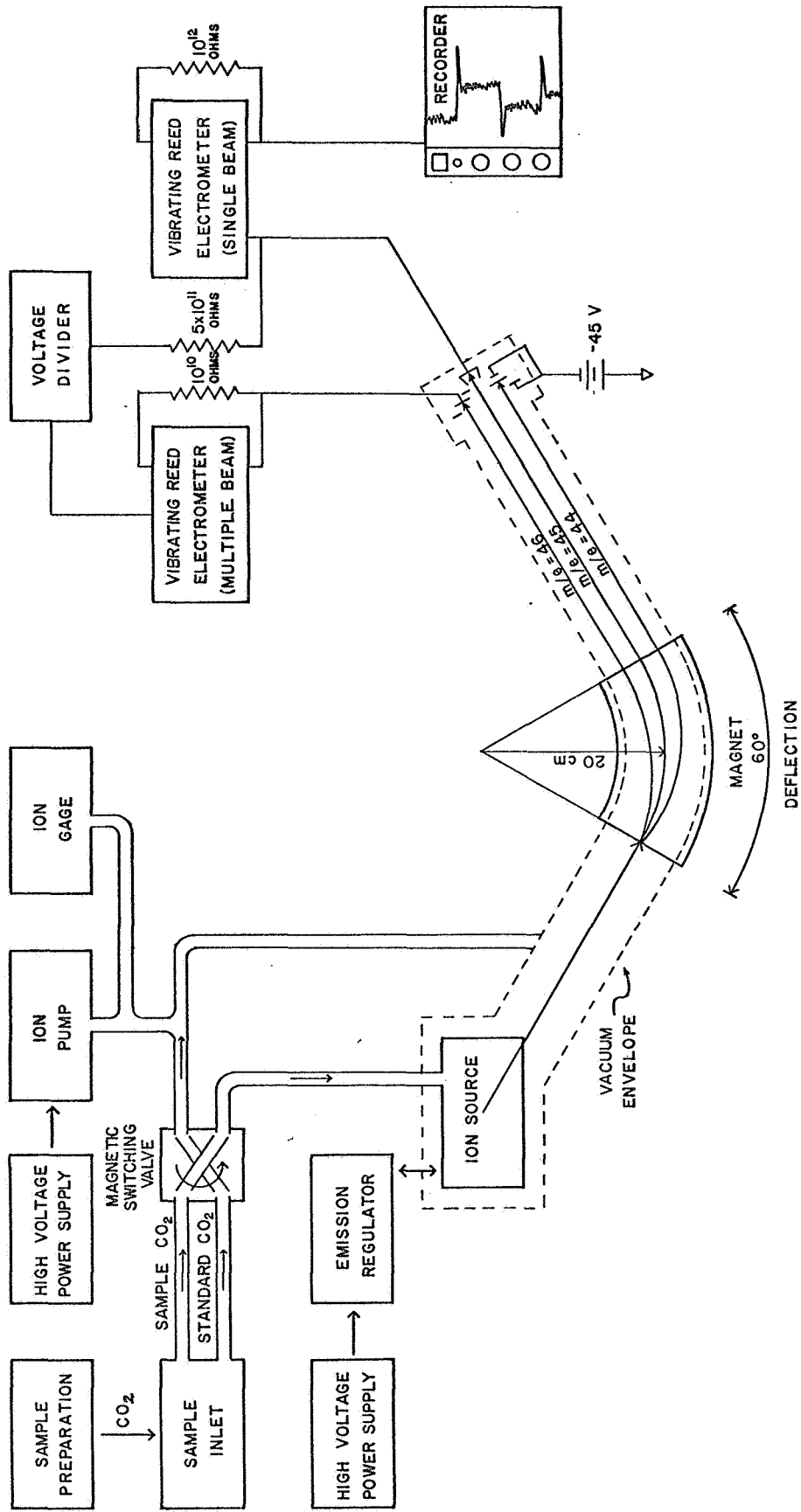
operate, less time consuming, and more reliable than previously reported instruments.

DESIGN AND CONSTRUCTION OF INSTRUMENTATION

Fundamental Principles of the Instrumental Technique

The measurement system is composed of three principal subsystems, a sample preparation subsystem, a sample inlet subsystem, and the gas analysis subsystem as shown in Fig. 1. The sample preparation subsystem contains a vacuum system, furnaces, pressure gauges, and distillation traps for burning samples under controlled conditions designed to convert all carbonaceous matter present to carbon dioxide. The sample inlet subsystem consists primarily of a pair of capillary leaks and a switching valve that directs first a standard carbon dioxide and then the unknown sample into the gas analysis subsystem. The gas analysis subsystem consists of a mass spectrometer and associated ratio recording electronics.

A standard gas is first directed into the mass spectrometer and the mass 44 ion beam composed of $C^{12} O_2^{16}$ is separated from the mass 45 beam which consists mostly of $C^{13} O_2^{16}$. A dual collector simultaneously collects both peaks separately. In the collector described in this paper mass 46 is also collected. The more intense, mass 44 ion current of the standard gas is divided by a calibrated precision decade voltage divider until the minor ion current of the mass 45 beam is nulled out. This null position is recorded on a potentiometric recorder. The sample of unknown isotopic composition is then directed into the ion source by actuating a gas switching valve. Any difference in isotope ratio will cause a deviation from the previously established null settings. This difference is determined by returning the system to a null position using the voltage divider and noting the new settings required to rebalance the system. This measurement is directly related to the difference in isotope ratios of a standard and an unknown gas. Results are usually reported as the difference, δ,

RECORDER

10^{12} OHMS

VIBRATING REED ELECTROMETER (SINGLE BEAM)

VOLTAGE DIVIDER

5×10^{11} OHMS

10^{10} OHMS

VIBRATING REED ELECTROMETER (MULTIPLE BEAM)

-45 V

$m/e = 46$
$m/e = 45$
$m/e = 44$

MAGNET 60°

DEFLECTION

20 cm

ION GAGE

ION PUMP

HIGH VOLTAGE POWER SUPPLY

MAGNETIC SWITCHING VALVE

SAMPLE CO_2

STANDARD CO_2

SAMPLE PREPARATION

CO_2

SAMPLE INLET

EMISSION REGULATOR

HIGH VOLTAGE POWER SUPPLY

ION SOURCE

VACUUM ENVELOPE

in parts per mil (o/oo) between the unknown gas and standard gas derived from a carbonate geological sample known as PeeDee Belemnite (PDB) where:
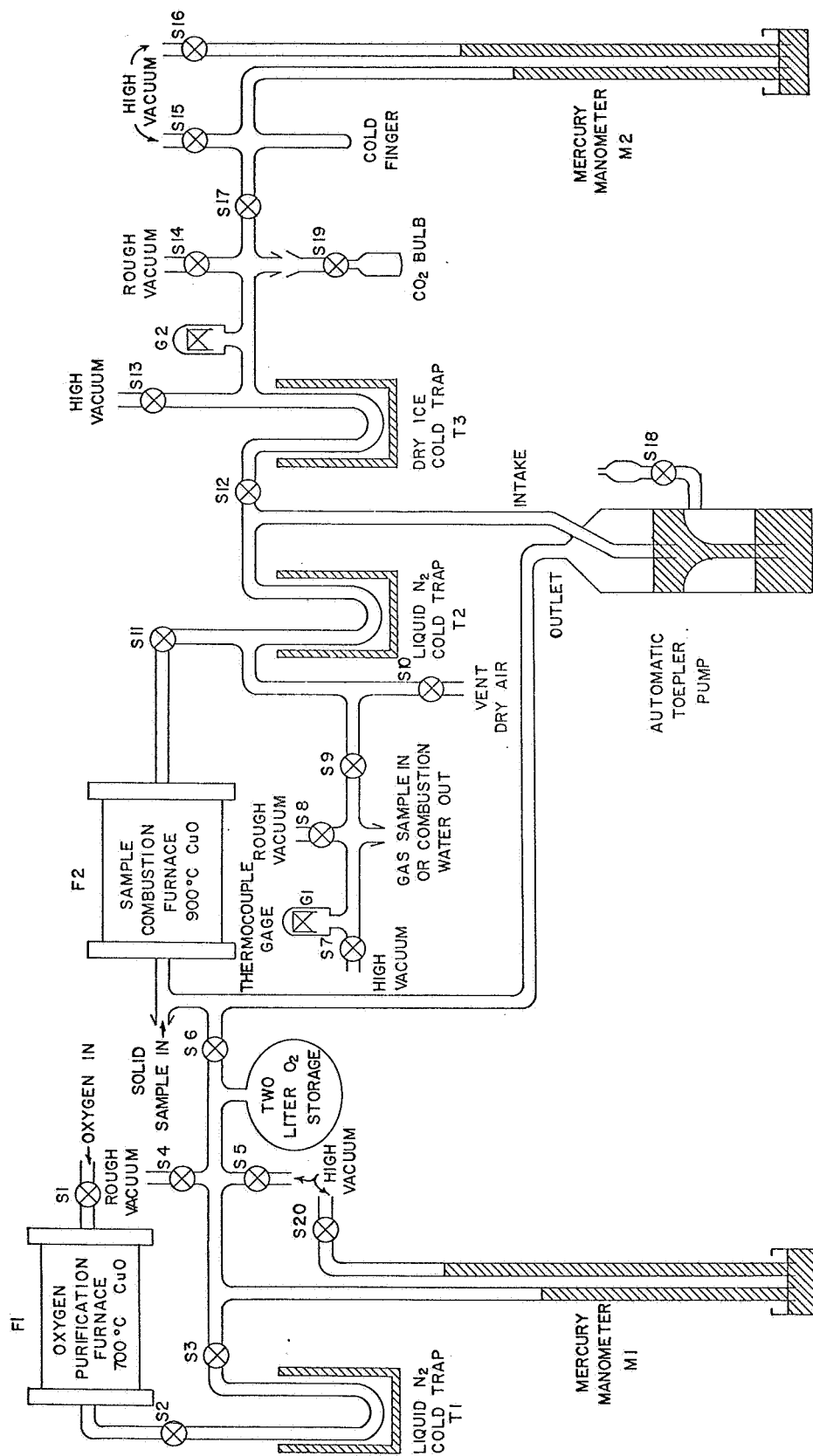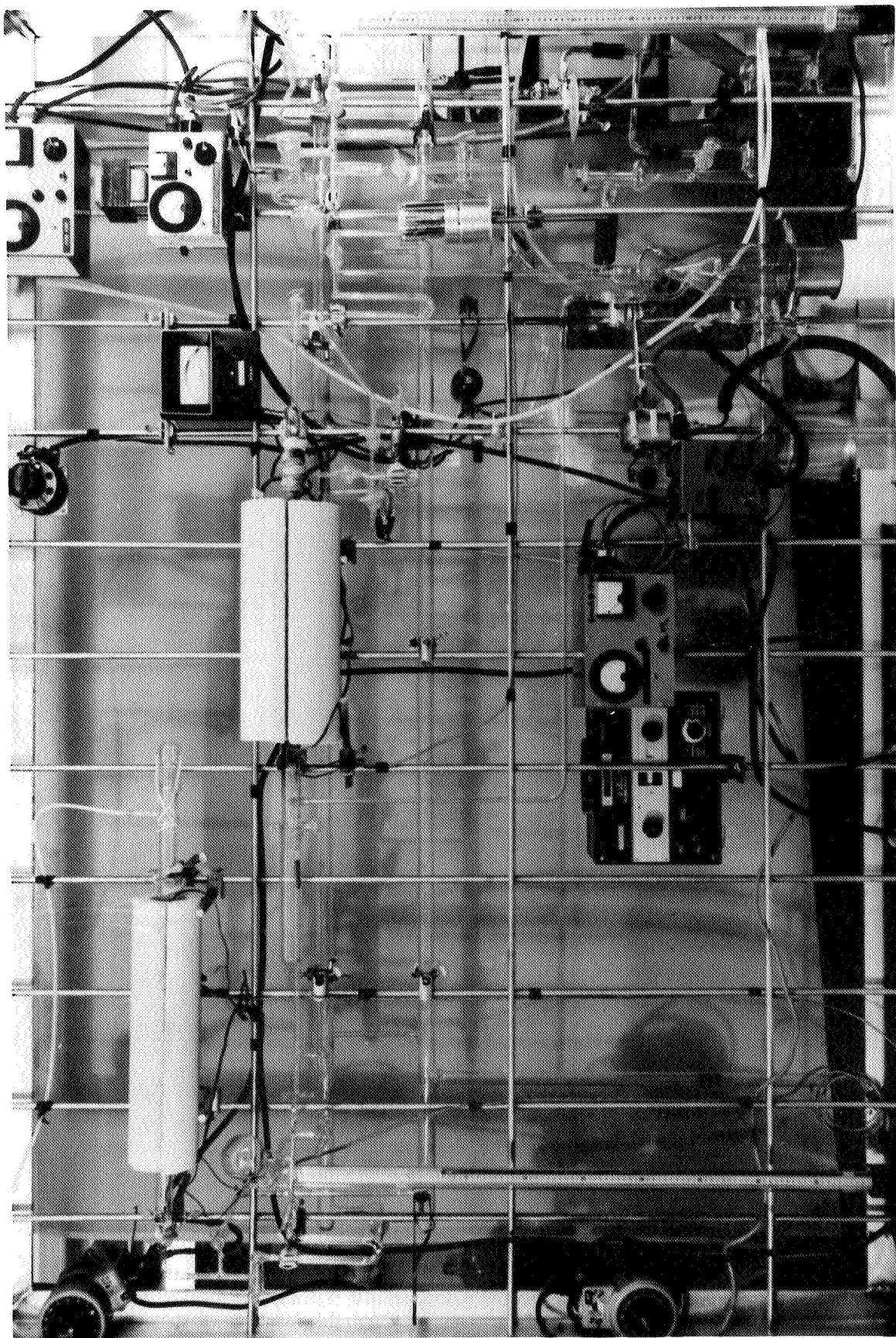
$$\delta = \frac{R_\mu - R_s}{R_s} \times 1000$$

R_μ = unknown voltage divider setting = C^{13}/C^{12}

R_s = standard voltage divider setting = C^{13}/C^{12}

Sample Preparation Subsystem

The initial step in making a stable carbon isotope ratio measurement is the conversion to carbon dioxide of the carbonaceous matter present in the sample. This provides a "working gas" which can then be introduced into the gas analyzer through a suitable sample inlet. The conversion is accomplished by combusting the sample over a catalyst at high temperature in an excess of pure oxygen and isolating the product carbon dioxide from the water and excess oxygen by fractional distillation. The most important single factor to be considered in sample preparation is the possibility of fractionating the sample and thereby causing a deviation in the measured isotope ratio from the true isotope ratio in the original sample. The surest way to prevent such fractionation is to completely combust all carbon in the sample and to quantitatively collect the product carbon dioxide. This can be insured by careful checks for complete combustion and by always freezing out the carbon dioxide to less than one micron pressure. An additional important consideration is the possible introduction of contaminants during sample handling and cross contamination between samples due to incomplete combustion.

Fig. 2 shows a schematic diagram of the vacuum system used initially for sample preparation which is similar to that described by Craig (7). The furnace tubes are one inch diameter fused quartz. This system consists of common readily available components as seen in the photograph of Fig. 3. Heating is controlled by a variable transformer or pyrometer controller. Low pressure measurements are made with an RCA 1946 thermo-

S16

S15

HIGH VACUUM

MERCURY MANOMETER M2

COLD FINGER

S17

ROUGH VACUUM

S14

S19

CO₂ BULB

G2

HIGH VACUUM

S13

DRY ICE COLD TRAP T3

S12

LIQUID N₂ COLD TRAP T2

INTAKE

S18

AUTOMATIC TOEPLER PUMP

OUTLET

S11

SAMPLE COMBUSTION FURNACE 900°C CuO

F2

THERMOCOUPLE GAGE

ROUGH VACUUM

S8

S9

S10

VENT DRY AIR

GAS SAMPLE IN OR COMBUSTION WATER OUT

G1

S7

HIGH VACUUM

OXYGEN IN

S1

ROUGH VACUUM

S4

SOLID SAMPLE IN

S6

S5

TWO LITER O₂ STORAGE

HIGH VACUUM

S20

OXYGEN PURIFICATION FURNACE 700°C CuO

F1

S3

LIQUID N₂ COLD TRAP T1

S2

MERCURY MANOMETER M1

couple gauge tube using a readout-control constructed in
the laboratory. The roughing vacuum consists of a 40
liter per min two stage rotary mechanical pump. The
high vacuum system consists of a 60 mm diameter three
stage mercury diffusion pump backed by a 280 liter per
min two stage rotary mechanical pump. This provides
sufficient pumping to evacuate the 1.5 liter volume of
the furnace and combustion train from atmospheric pres-
sure to less than one micron in approximately three min-
utes.

The above described sample preparation subsystem
involves a complex operational procedure and requires a
relatively complicated vacuum system. The use of a
Toepler pump is fraught with many difficulties, the most
undesirable being the formation of mercury "hammers" if
atmospheric leaks develop. This actually occurred during
the course of the work described here and resulted in
mercury being driven into the hot sample combustion fur-
nace. It was also difficult to obtain reproducible
results using the above sample preparation system, but
this may have been due to a leaky combustion tube. In
order to simplify the sample preparation procedure and
provide a more reliable technique, an alternate sample
preparation subsystem was designed and constructed. It
should be noted, however, that the older Craig-type
sample preparation technique is used in most laboratories
and gives good results.

A schematic diagram of the alternate sample prep-
aration subsystem is shown in Fig. 4. Tank oxygen is
admitted to this system with no purification. Results of
sample runs given in Table I indicate there is no signif-
icant effect on reproducibility when oxygen purification
is omitted. The system is constructed of Pyrex glass.
The furnace is a standard model 8-in. Hevi-Duty combus-
tion furnace controlled by a pyrometer controller. It is
capable of reaching the operating temperature of $900^{\circ}C$ in
15 mins. The thermocouple gauge, rough vacuum and high
vacuum components are described previously for the Craig-
type subsystem. The combustion tube is Vycor and is
shown in detail in Fig. 5. The silver is positioned to
maintain a temperature of $550^{\circ}C$ while the sample is at
$900^{\circ}C$ in the center of the furnace body. The tube is
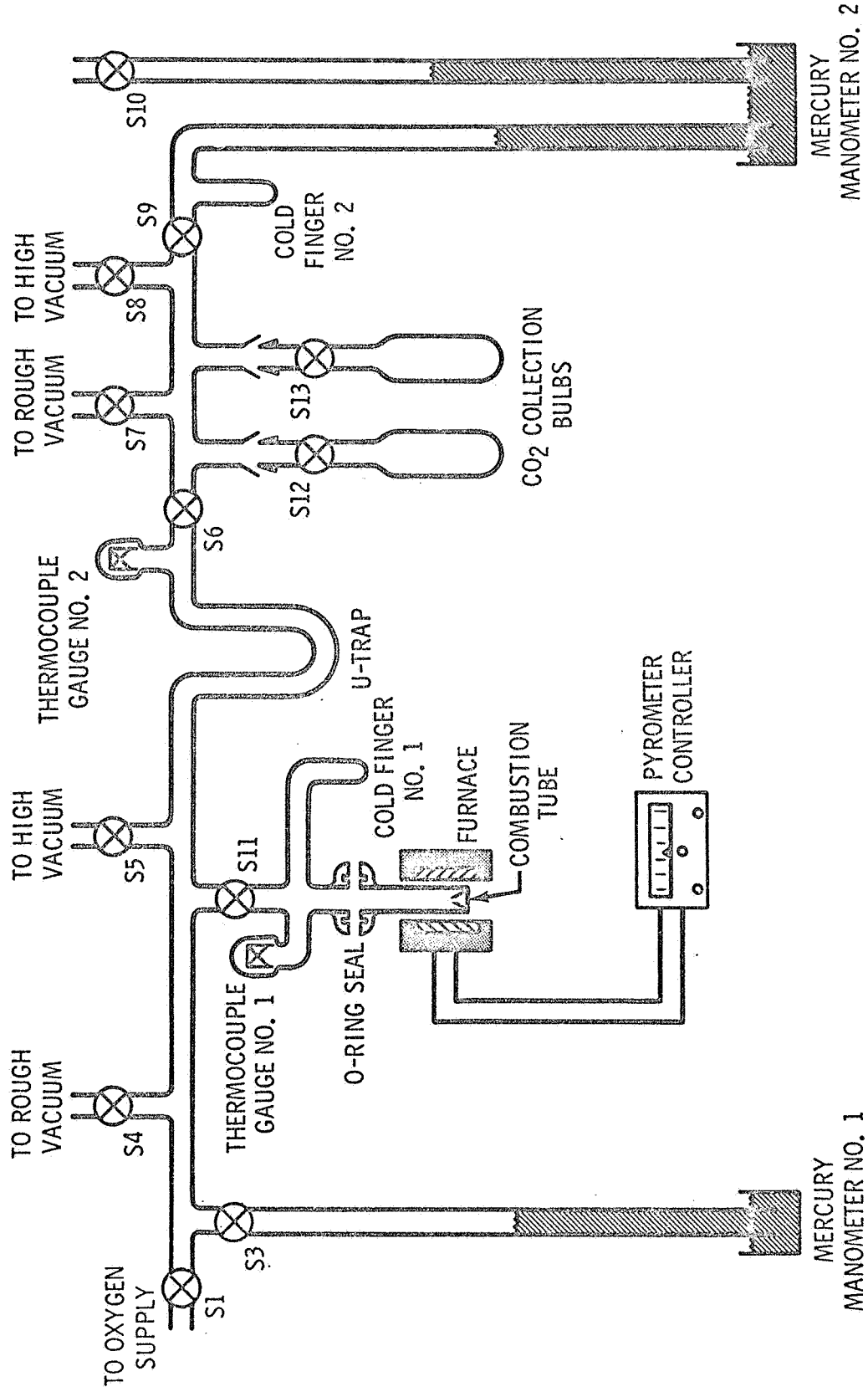sealed to the O-ring seal through a graded joint. The

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TABLE 1

EFFECT OF OXYGEN PURIFICATION ON PRECISION

Sample	Oxygen Treatment	Measured δC^{13} (o/oo)*	Avg. $\pm$ Std. Dev.
NBS Oxalic Acid	Purified	+21.61	
NBS Oxalic Acid	Purified	+21.66	
NBS Oxalic Acid	Purified	+21.56	
			+21.61 $\pm$ 0.05
Graphite	None	−21.59	
Graphite	None	−21.46	
Graphite	None	−21.47	
			−21.51 $\pm$ 0.07

* δC^{13} relative to a gas of unknown isotopic composition placed in the sample side of the capillary inlet leaks.
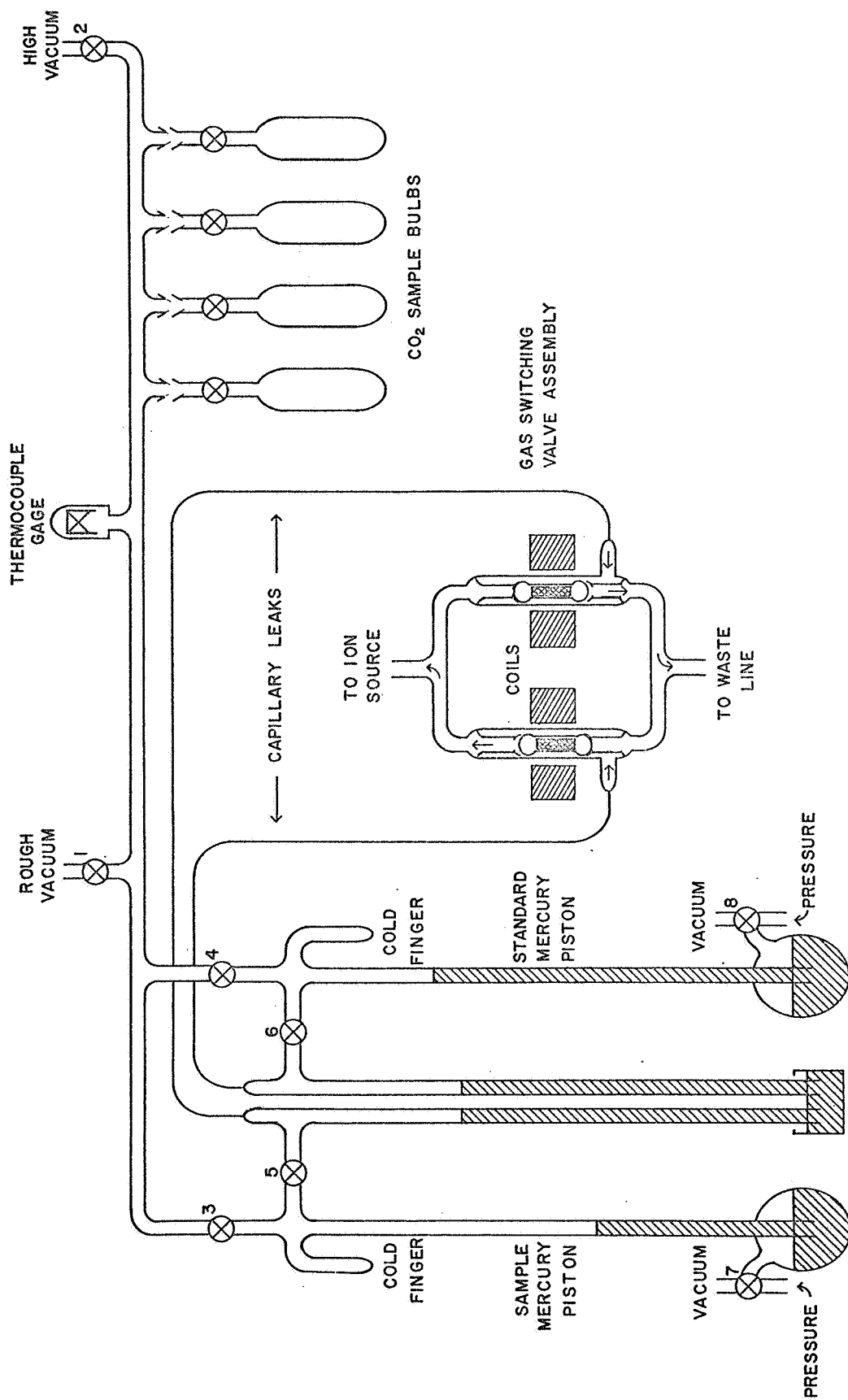
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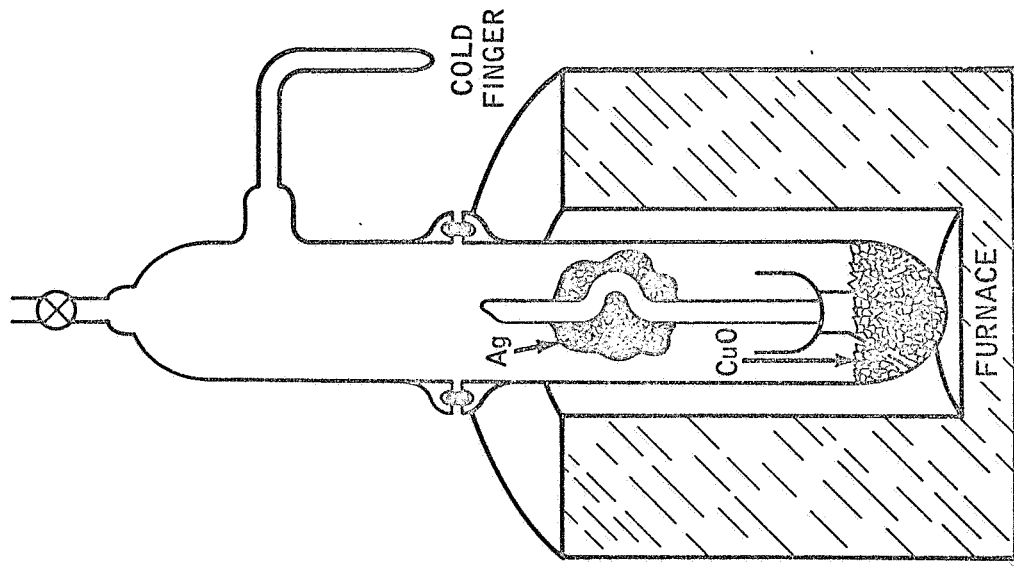
O-ring seal is made by Corning and requires only a very minimal amount of grease. The copper oxide was prepared as before and the silver wool can be purchased from most chemical suppliers.
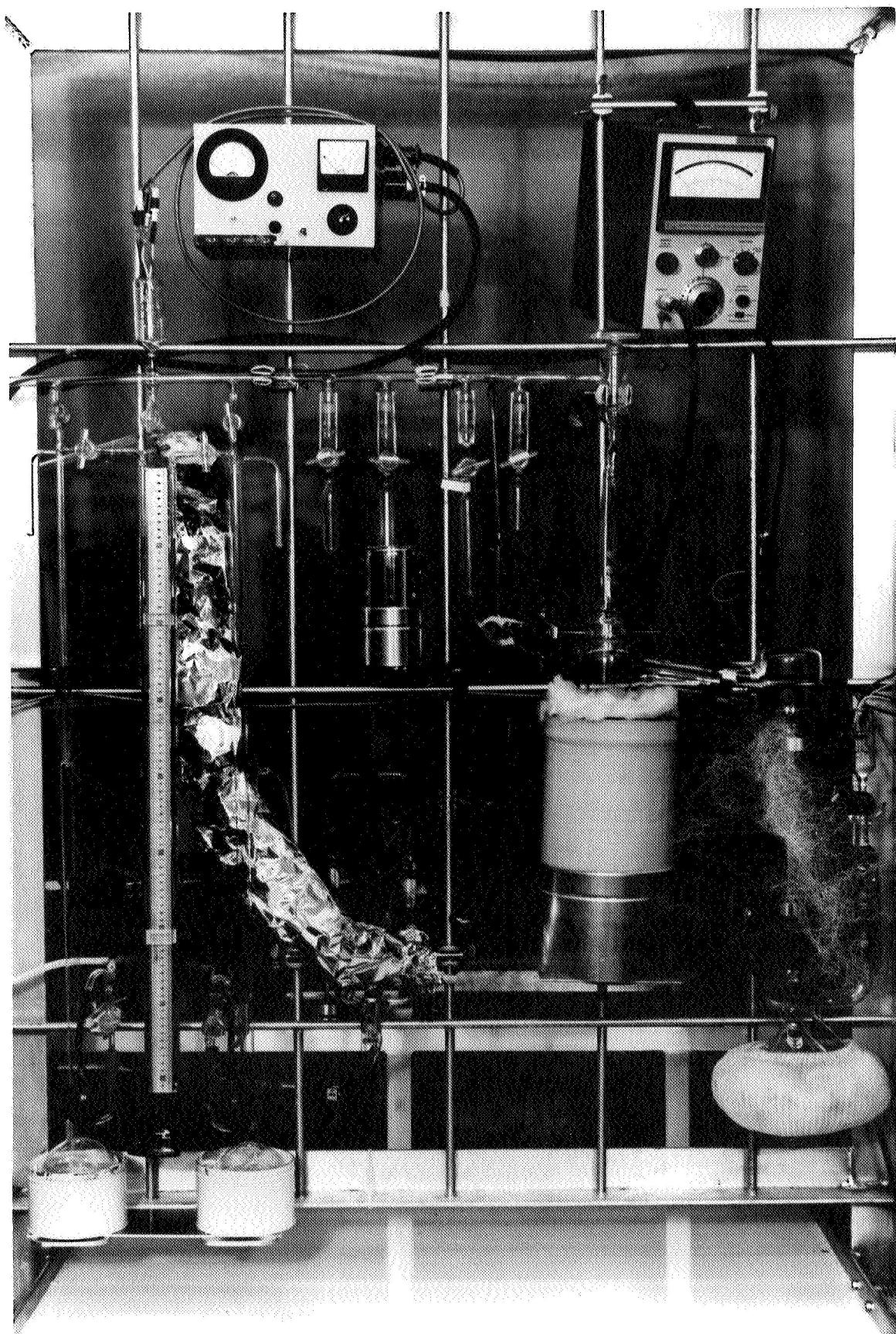
Sample Inlet Subsystem

The sample inlet subsystem which serves to introduce the carbon dioxide to the mass spectrometer under carefully controlled and reproducible conditions, is shown schematically in Fig. 6 and as constructed in Fig. 7. The vacuum system is identical to that for sample preparation. The mercury levels in the pistons are controlled by two way stopcocks on the reservoirs. Pressures greater than one atmosphere are obtained by pipette bulbs when necessary. The capillary leaks and the gas switching valve assembly are the critical points in this subsystem. The coils which energize the switching valves must be constructed so that the valves close tightly but do not strike the seat so hard as to cause chipping after repeated use. The coils in the valve's used in this study were wound in the laboratory and are two inches in height and contain 800 turns of 22-gauge wire. The coils are actuated by a power supply providing 110 mA at 100 volts. The capillary leaks constructed of soft annealed nickel are 0.004 in. i.d (0.030 o.d) and 30 in. in length. They are sealed into the Pyrex glass with Kovar seals. The leaks are wrapped with glass wool and aluminum foil insulation to maintain thermal stability as flow through the leaks is highly dependent on temperature. The insulation was necessary because the air conditioning outlet blows directly onto the leaks. A heating tape is buried in the insulation for baking the leaks at periodic intervals which aids considerably in reducing the noise level when recording ratios. Since the measured ratio can vary with total ion beam intensity, fluctuations in gas flow cause drift of the ratio null position and must be avoided. A thermostatted oven housing the leaks is, therefore, preferred.

Mass Spectrometer Instrumentation

In this section a detailed description of the mass

HIGH VACUUM

CO₂ SAMPLE BULBS

GAS SWITCHING VALVE ASSEMBLY

THERMOCOUPLE GAGE

CAPILLARY LEAKS

TO ION SOURCE

COILS

TO WASTE LINE

ROUGH VACUUM

COLD FINGER

STANDARD MERCURY PISTON

VACUUM

PRESSURE

COLD FINGER

SAMPLE MERCURY PISTON

VACUUM

PRESSURE

spectrometer of the isotope ratio measurement system is presented. The photographs, Figs. 8 and 9, show the completed apparatus. The individual drawings and schematics demonstrate the economy and simplicity of the mass spectrometer. Of necessity, the description of the mass spectrometric instrumentation is further broken down into smaller subsystems including (1) the fundamental ion optics, (2) the vacuum system and its related accessories, (3) the ionizer, (4) the ionizer (ion source) control, (5) the ion beam focus and direction control, (6) the ion accelerating energy supply, (7) the ion beam momentum separating magnet, (8) the dual ion collector, and (9) the dual ion current null ratio measurement and display system. The following discussion of this apparatus not only shows the uniqueness of some of the components, but also provides for the first time a single unified explanation to the whole isotope ratio mass spectrometer instrumentation.

Fundamental ion optics. - The fundamental ion optics are applicable in general for all momentum focussing mass spectrometers. In the particular case of this instrument the 60 degree deflection, 20 cm radius, normal entry, symmetrical system was chosen. The source slits were set at 0.33 mm while the collector slits were set at 1.14 mm Electrical beta axis direction focus plates were used to improve sensitivity and to facilitate optical alignment. The mechanical superstructure was constructed to accommodate these parameters.

The above choices were based on the fact that the masses to be separated are 44, 45, and 46, and further, that these associated ion beams must have wide flat tops and no contribution of one to the other (often referred to as "tailing"). In the conventional sense, resolution becomes meaningless and dipersion and stability become the dominating factors. Considering the basic equation for the ion trajectory in a magnetic instrument as conven-

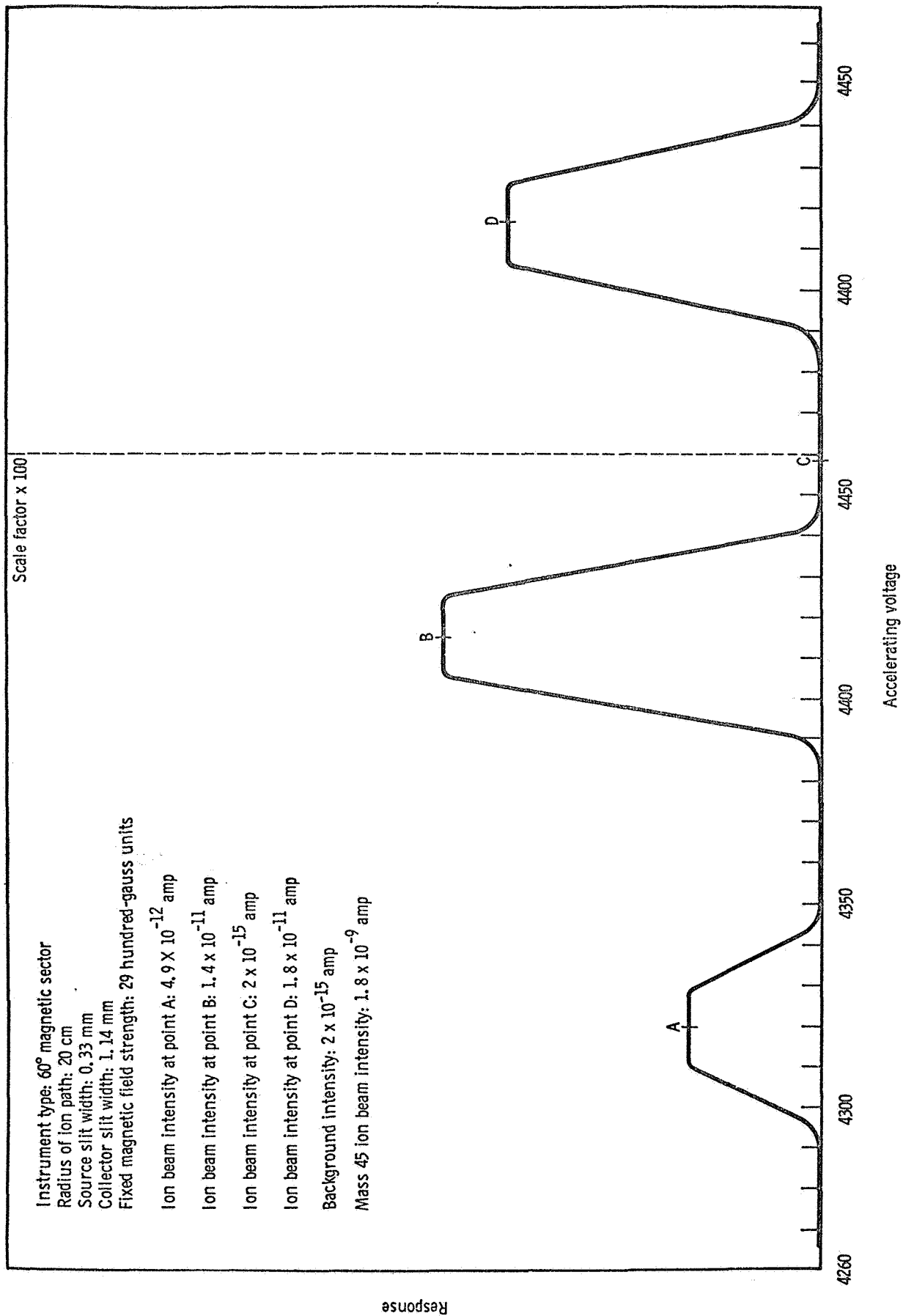$$m/e = k \ \frac{r^2 \beta^2}{2V}$$

tionally defined, the results of this instrument were such that for $C^{12}O_2$ mass 44 and $C^{13}O_2$ mass 45; r equals 20 cm, e and k are approximately unity, β becomes 29
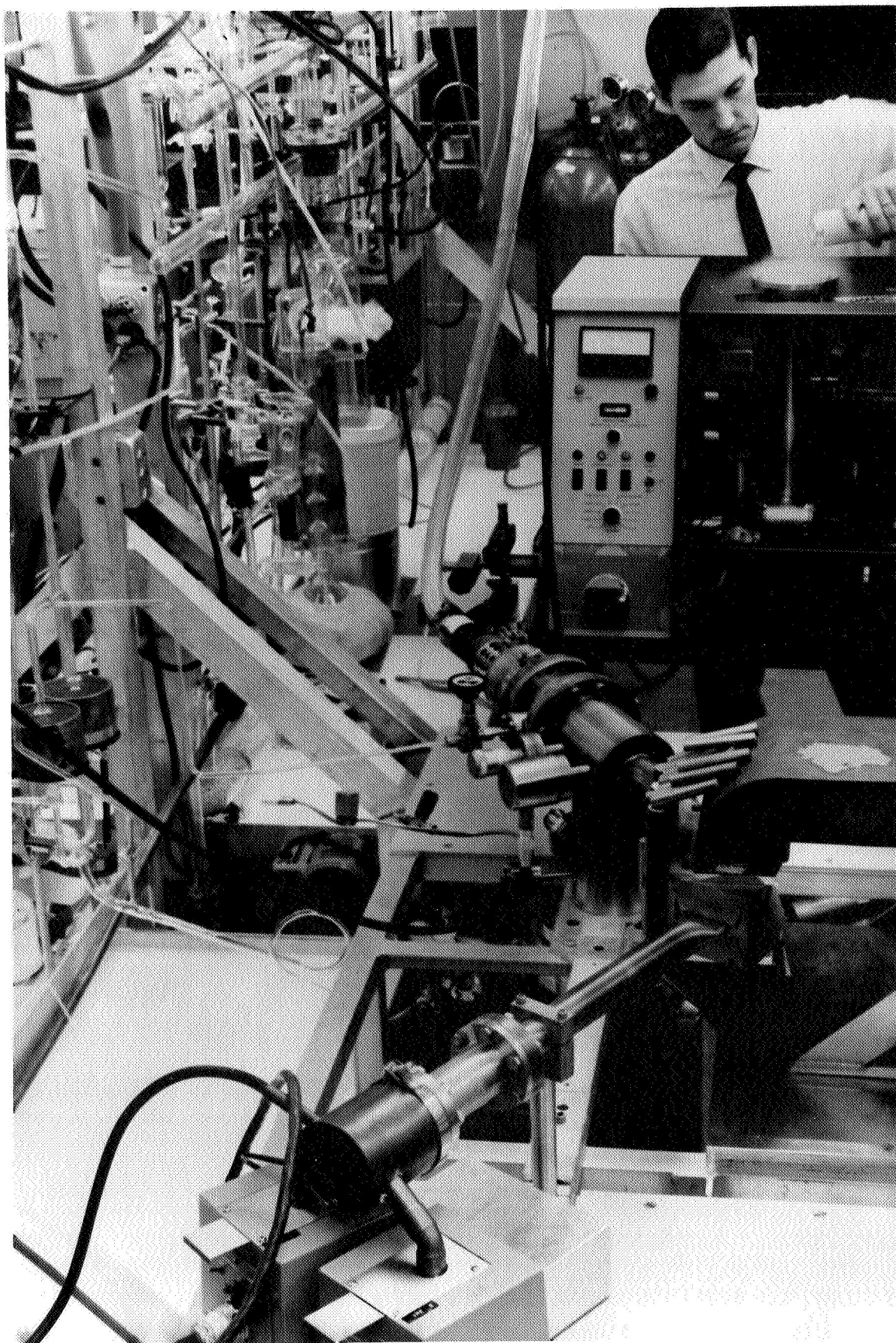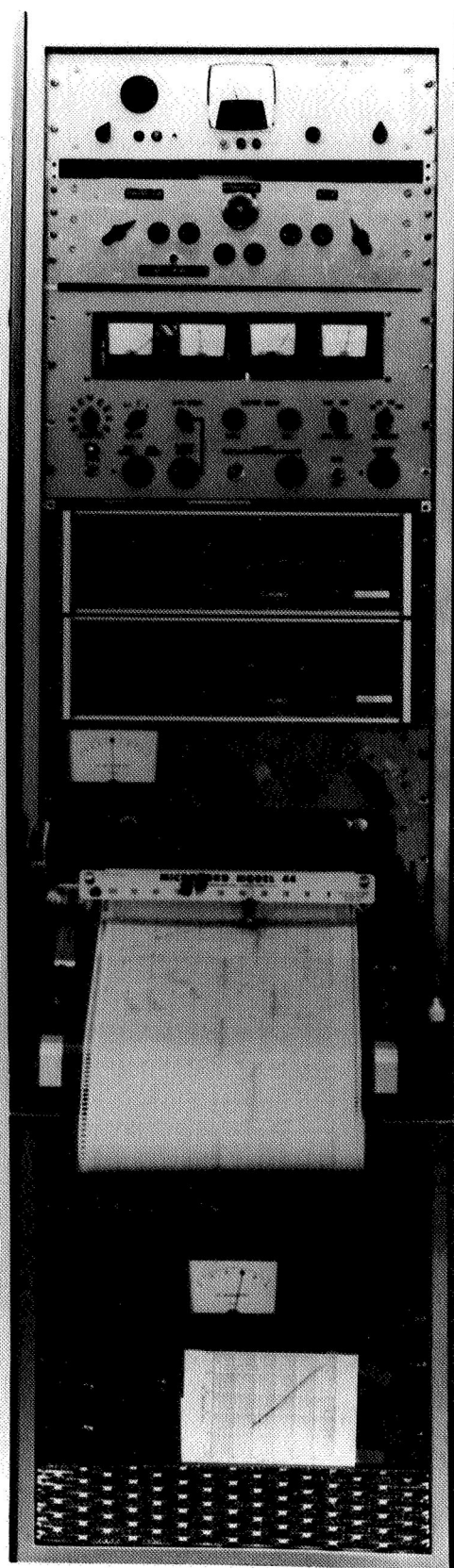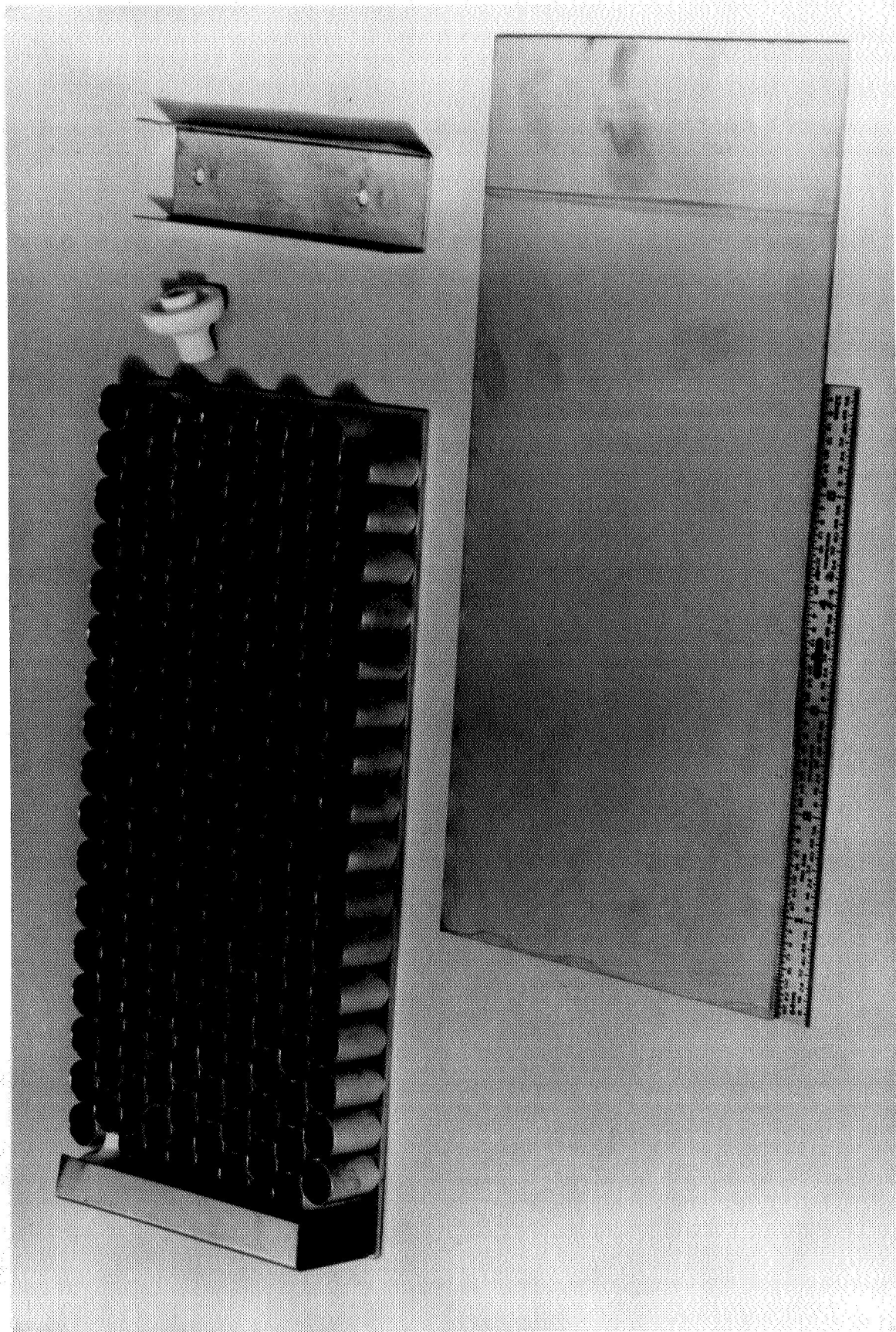
hundred-gauss units, and V for mass 45 was 4414 volts while V for mass 46 was 4320 volts as shown in the voltage response plot of Fig. 10. The mass 45 ion beam peak showed no measurable change in intensity over a 26 volt range in V and no measurable contribution of mass 44 to mass 45 was encountered. The ion beam intensities given are typical of those obtained in the measurements of ratios.

The vacuum system. - The vacuum system is truly ancillary. The system and its related accessories evolved from the basic needs for pumping speed, no contamination, sufficient mean free path, and care free operation. Stainless steel and conventional copper gasket seals were used whenever possible. A cold cathode sputter ion pump was constructed. The internal assemblies of this pump are shown in the photograph, Fig. 11. The essential design parameters are 330 stainless steel cylindrical anode cells 1/2 in. in diameter by 3/4 in. in length with a wall thickness of 0.015 in. in an electric field of nine kV and a magnetic field of 25 hundred gauss units. The cathodes are constructed of standard type 25A titanium plates 1/16 in. thick. Ceramet speaker type magnets were used to produce the magnetic field and a power supply was designed and constructed to produce the electric field. The power supply is shown at the bottom of photograph in Fig. 9, and in the schematic diagram, Fig. 12. A neon-sign type transformer with a 15 kV secondary center tapped is connected to a typical full wave rectifier assembly using two strings of F-6 type diodes. This approach is quite simple and very adequate for this pumping system. Typical unbaked pressures in the low 10^{-8} torr region were achieved even though this pump was used for both the sample and the waste lines. The pressure was measured by a thoriated/iridium all metal Bayard-Alpert gage tube controlled by a General Electric type GC130 controller as shown on the top of the photograph in Fig. 9. A vacuum protect relay triggered by the gauge readout circuit turns off the ion source if a pressure surge drives the readout off scale. The indicated pumping speed is about 450 liters per sec. Even though little care was given to special cleaning, bakeout of the vacuum system was never necessary even after samples containing sulfur had been run. The simplicity and capability of the vacuum system played a major role in

Scale factor x 100

Instrument type: 60° magnetic sector
Radius of ion path: 20 cm
Source slit width: 0.33 mm
Collector slit width: 1.14 mm
Fixed magnetic field strength: 29 hundred-gauss units

Ion beam intensity at point A: 4.9×10^{-12} amp

Ion beam intensity at point B: 1.4×10^{-11} amp

Ion beam intensity at point C: 2×10^{-15} amp

Ion beam intensity at point D: 1.8×10^{-11} amp

Background intensity: 2×10^{-15} amp

Mass 45 ion beam intensity: 1.8×10^{-9} amp

Response

Accelerating voltage

4260   4300   4350   4400   4450   4450   4400   4450

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rapid carefree operation of the mass spectrometer.

Ionizer. - The ionizer, or more commonly, the ion source assembly, was adapted from an Atlas-Werke type electron bombardment chemical analytical unit. This is basically a Neir configuration with modifications for organic chemistry. Electrons were produced from a rhenium filament, focused into the ionizing region with a 5 volt negative lense, and collimated with small internal permanent magnets. Draw out plates were used in place of repeller plates. Figs. 13 and 14 are close up views of the actual ion source.

Although internal heaters with a platinum sensor were available they were not used for the carbon isotope work. Adjustable ion collimating slits and beta direction focussing electrodes were part of the analyzer tube. In spite of the fact that this is a very unorthodox ion source for an isotope ratio difference mass spectrometer, its performance was quite adequate and was in no way a limiting factor. The electrical connections to the electronics console were housed in a shielded plastic garden hose and intended for possible 10 kV operation.

Ionizer control. - The ionizer control (shown above the Cary electrometers in Fig. 9) or emission regulator design and construction constituted a major effort and is treated in detail on the schematic diagram, Fig. 15. Essentially the design objectives included the most stringent requirements for both analytical applications and isotope ratio difference work. For this reason it is considerably more complex than necessary for either single application. The basic circuitry is patterned after the LKB Productor Model 9000 unit. However, it was re-engineered to provide for domestic components, greater stability, easier service, and improved reliability. The fundamental approach consists of a transistorized multivibrator unit to provide 4 kH$_z$ alternating current to drive the entire remaining emission controller subassemblies. The sub-assemblies included dual variable electron energy control, trap current regulation, filament drive power, temperature measurement coupled to the proportional source heater, and variable electron lens potential. The general engineering approach employed solid state circuitry and achieved very low noise levels

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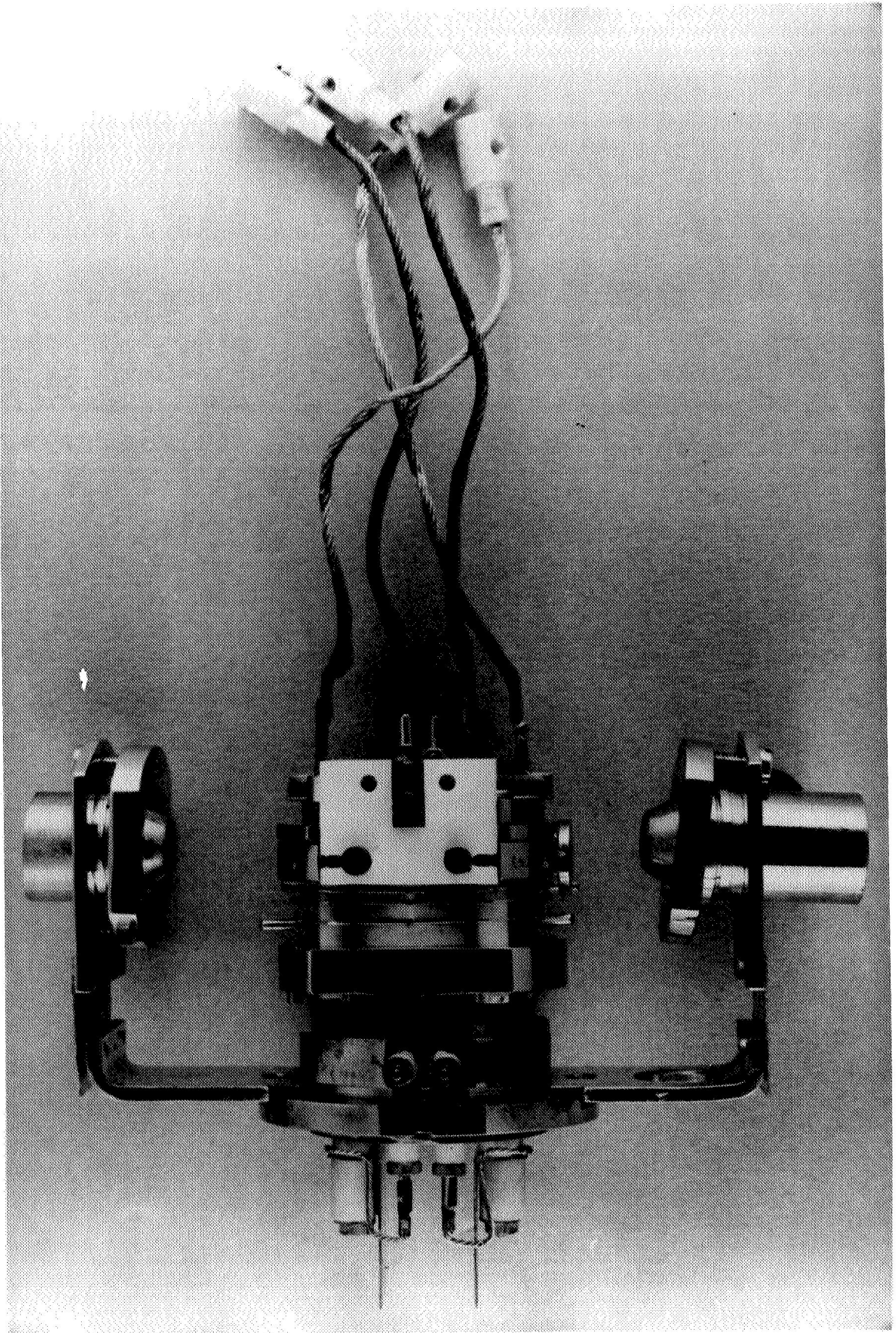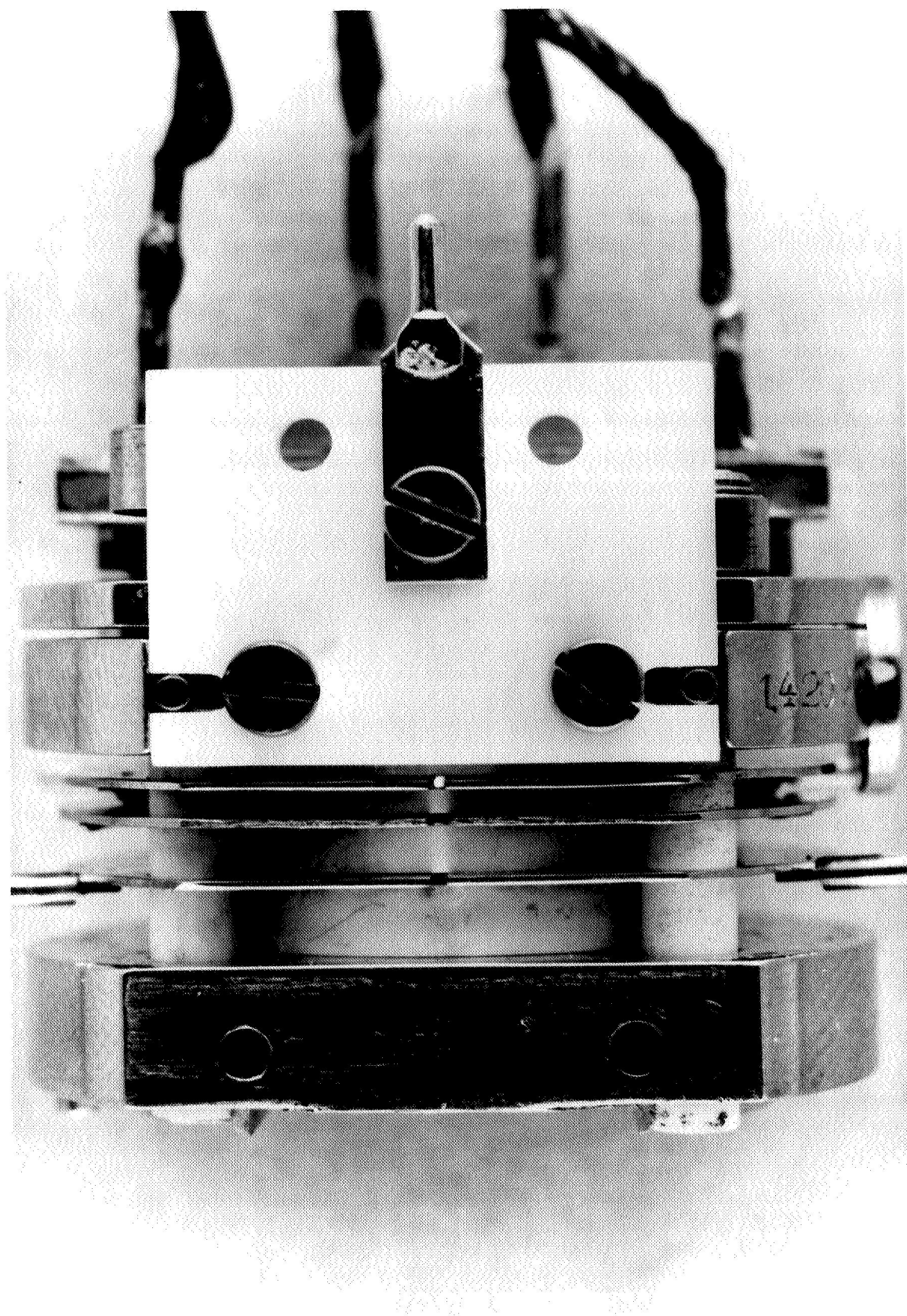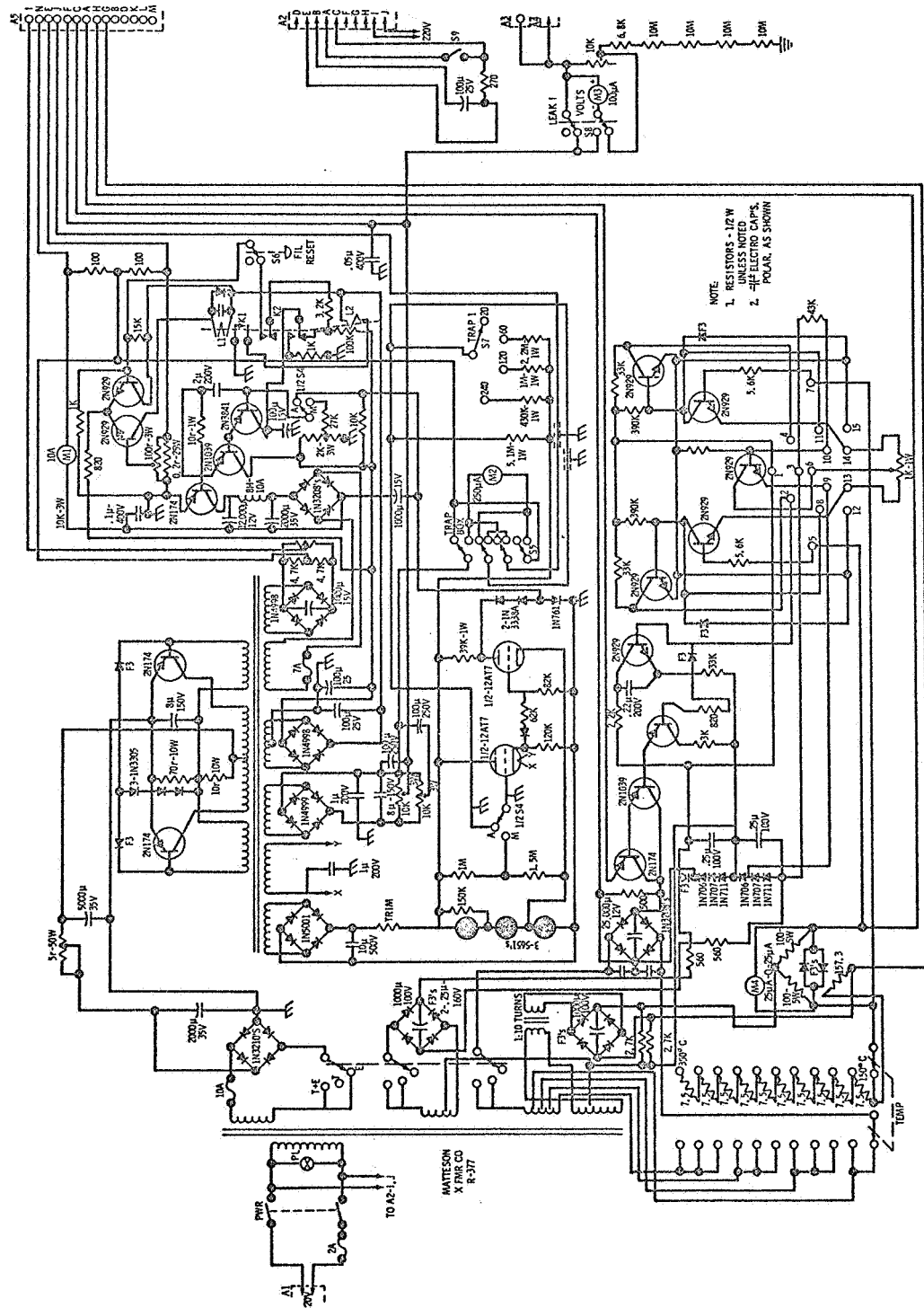
along with the other desired results.

Ion beam focus and direction controller. - The ion
beam focus and direction controller is shown between the
emission regulator and the vacuum gauge controller in the
photograph, Fig. 9. This unit is a simple resistance
voltage divider network to provide the drawout, alpha
direction focus potential and beta direction focus poten-
tial. Large capacitors were provided to minimize the
effects of noise pickup. In general, this, just as the
emission regulator, was built to provide for other possible
applications of the mass spectrometer. Due possibly to
inadequate resistor quality, the drawout potentials, once
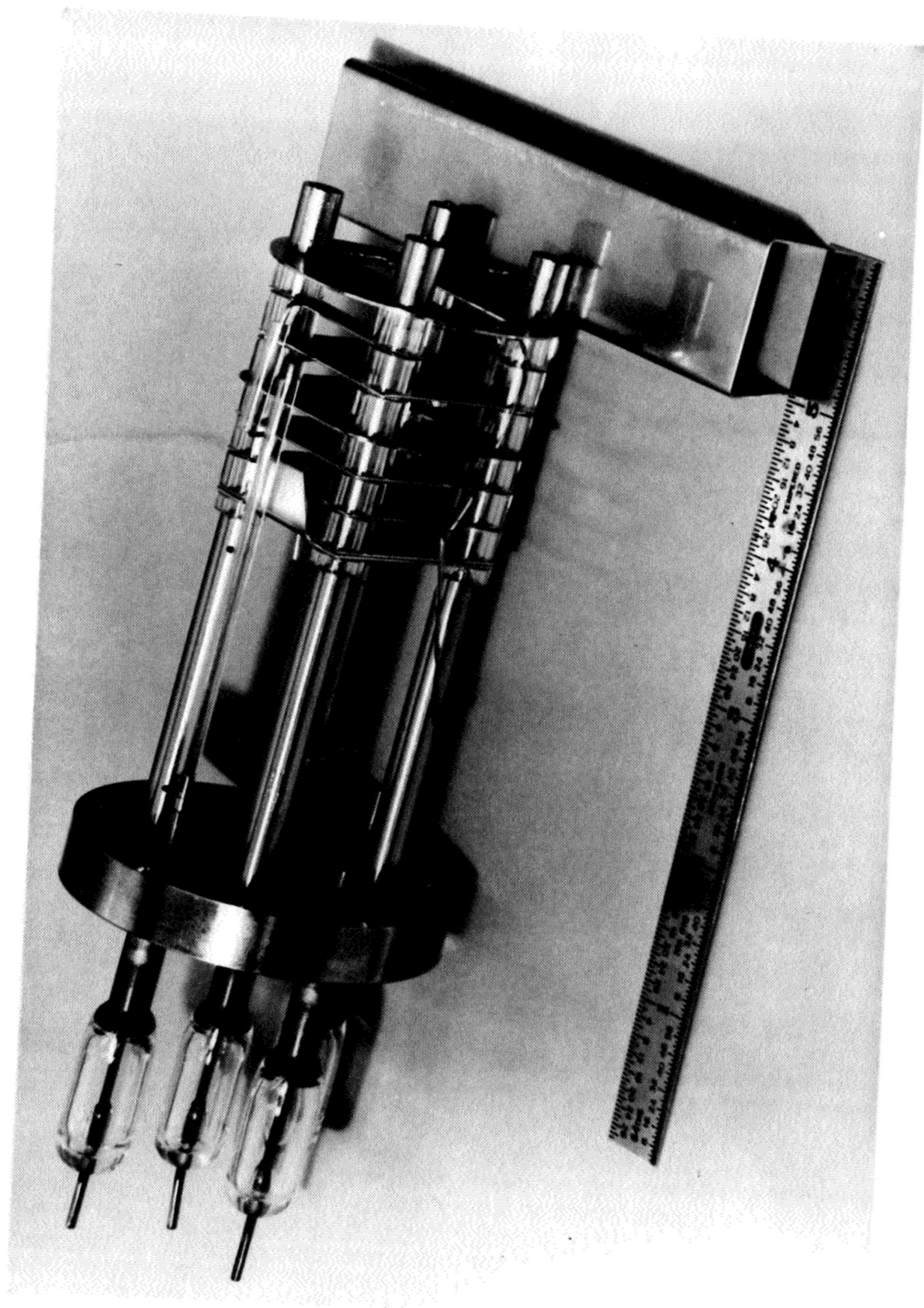optimized do not remained fixed from day to day.

Ion accelerating energy supply. - The ion accel-
erating energy was provided by a standard John Fluke type
408-B high voltage power supply. This unit meets or
exceeds all the basic electrical requirements to provide
necessary ion energy. During the first start up of the
mass spectrometer, it is convenient to be able to scan
the mass spectra. This was not easily possible because
the power supply is step controlled and the deflection
magnet used was a permanent magnet; therefore, the initial
test phases were somewhat tedious. Once normal isotope
ratio procedure was established, the inability to mass
scan was of no consequence. The other advantages of this
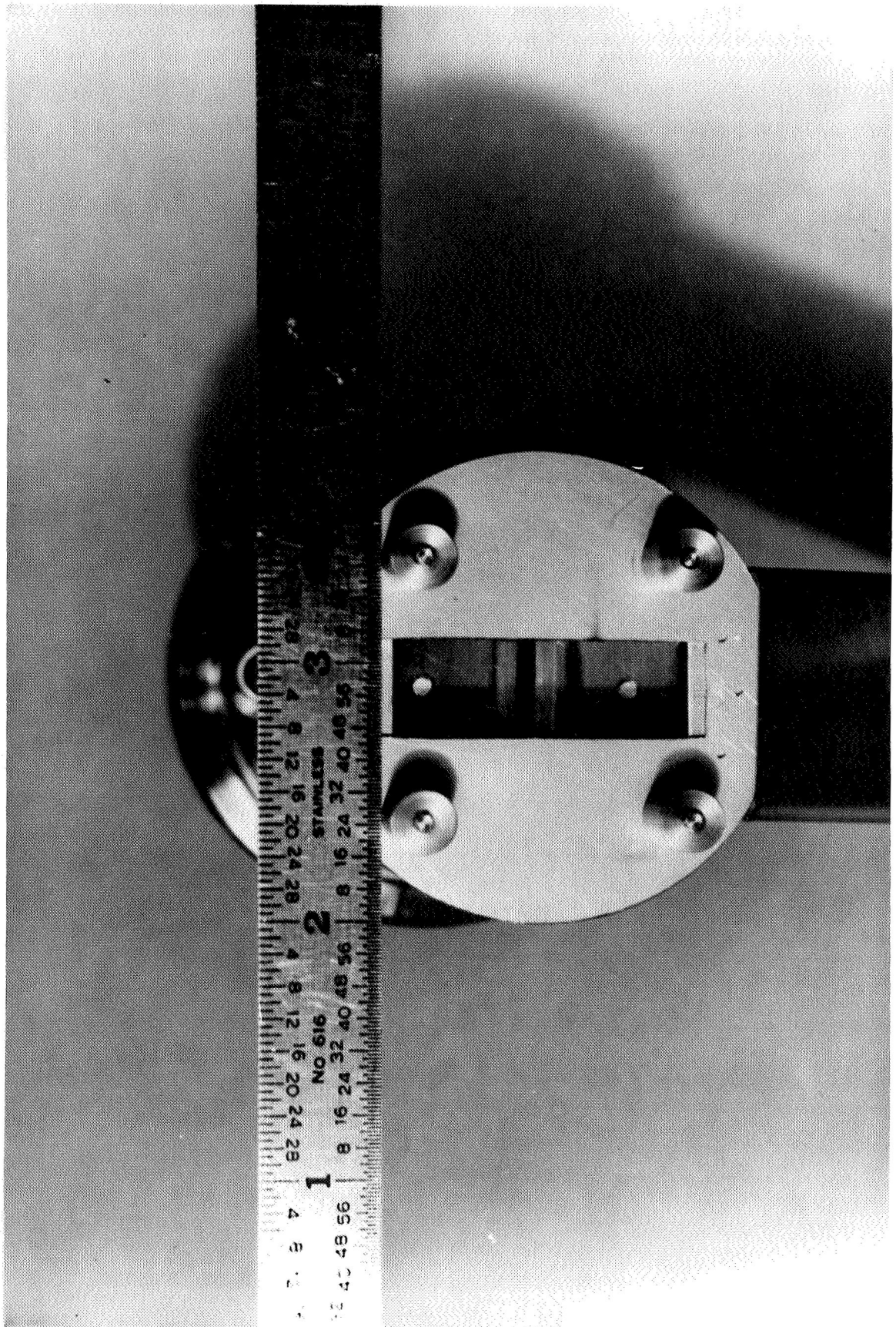unit more than offset this shortcoming.

Ion beam momentum separating magnet. - The main ion
beam momentum separating magnet was constructed from an
Alnico VIII permanent magnet. The assembly is shown on
the analyzer section photograph, Fig. 8. The original
basic magnet had a gap distance of about 3 5/16 in. and
an area of 4 1/4 by 7 in. as defined by the two 1/2 in.
thick soft iron pole cap plates. In the center of this
gap a field of 22 hundred gauss was measured. A set of
special pole pieces was designed and constructed to fit
within the gap and provide the proper magnetic field for
the $60°$ 20 cm momentum separator geometry. These special
caps had a 1 cm gap, a 20 cm mean radius, a 16.5 cm inner
radius, a 23.5 cm outer radius, and a $60°$ sector. Thus
the ion entrance and exit faces were at $60°$ angles to
each other, normal to the ion beam, and were 7 cm wide.
The caps were tapered on both the inner and outer radial

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faces up to a 10 cm width and mounted on the 1/2 in. thick
original pole cap plates. These special pole caps were
machined on a lathe from a single ring of type J-20 mild
steel, then the two 60° sectors cut out. This machining
technique proved remarkably economical and quite satisfac-
tory. The original design approach was to provide the
maximum uniform magnetic field throughout the required
volume with the given permanent magnet and through adjust-
ments of the ion energy accordingly to place mass 45 in
the principal focus. However, several factors forced an
alternate approach bearing in mind the fact that a max-
imum ion accelerating voltage is desirable for all opera-
tional performance parameters. First, the resulting
magnetic field within the special pole caps turned out to
be a 48 hundred gauss and secondly when the ion accel-
erating energy exceeded 6 kV arcing occurred in either the
ion source or the ion source feed through. This forced
us to shunt the magnetic field down to 29 hundred gauss
by means of 1/2 in. diameter soft iron rods as shown in
the photograph, Fig. 8. Fortunately, field uniformity
was retained and mass 45 was then located at 4414 volts.
The ease and simplicity of construction and mounting of
this main magnet did not compromise the ion optics in any
way and contributed much to the rapid and econimical
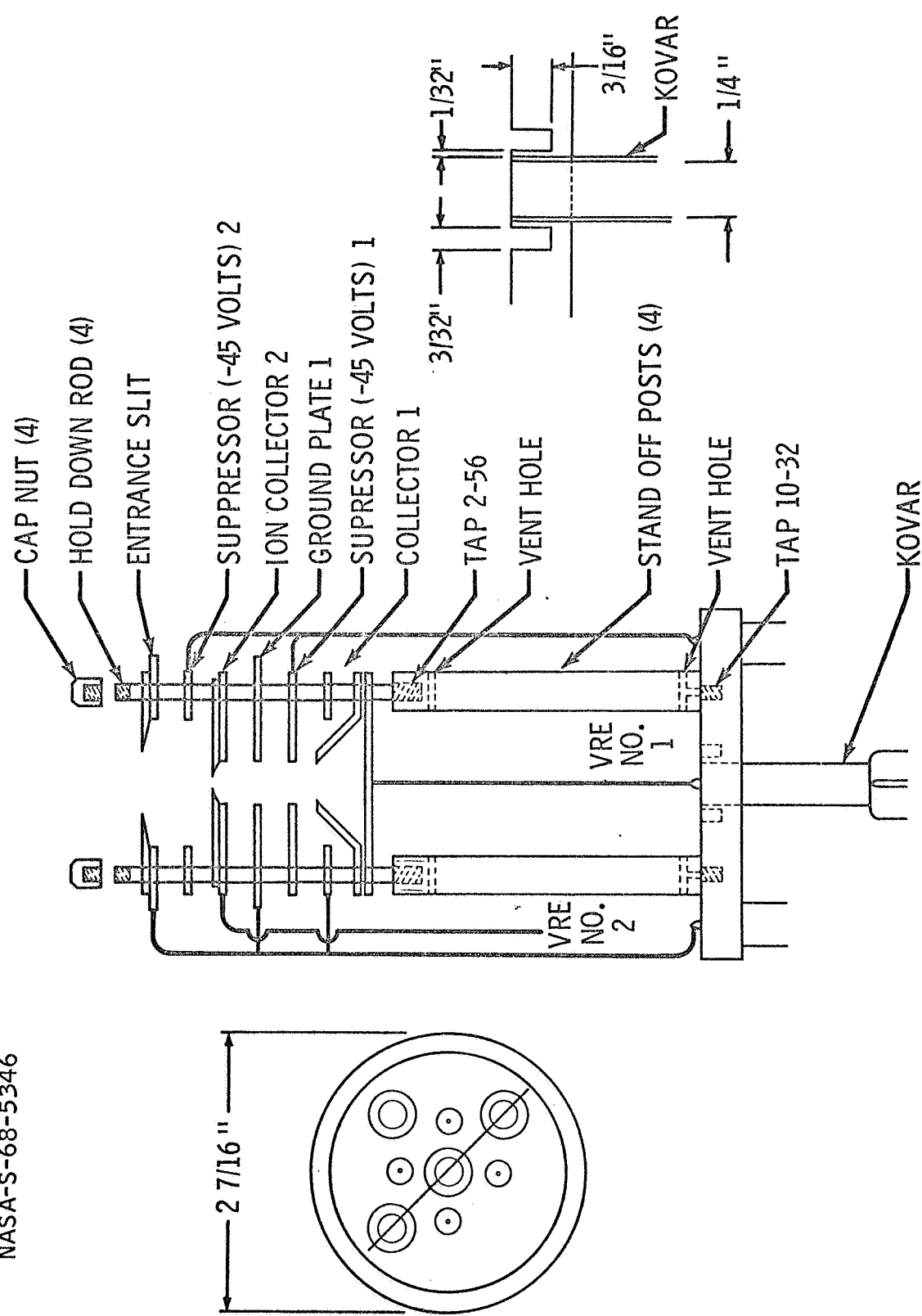construction of the mass spectrometer.

Dual ion collector. - The dual ion beam collector
assembly is shown in the photograph, Fig. 16, and the
diagram, Fig. 17. A Faraday cup arrangement is used for
the minor ion beam (mass 45 or 46) at the principal focus
point while a simple flat plate is used for the multiple
collector. Each collector is shielded with ground rings
and also with 45 volt supressor electrodes. The stainless
steel internal parts were cleaned by dipping in a mixture
of 3% hydrofluoric 40%nitric acid prior to assembly.

The collector view shown on the photograph, Fig. 18,
is from the ion source end and shows the ion burn of mass
44 after a brief check out period. From this the disper-
sion is easily shown, as is the fact that perfect focus
was not present. Raising the collector slightly corrected
the focussing problem and the collector was never again
removed. The electrical connectors to the ion collector
are very critical and must provide a low noise level and
a minimum contact potential. This was accomplished by

CAP NUT (4)

HOLD DOWN ROD (4)

ENTRANCE SLIT

SUPPRESSOR (-45 VOLTS) 2

ION COLLECTOR 2

GROUND PLATE 1

SUPRESSOR (-45 VOLTS) 1

COLLECTOR 1

TAP 2-56

VENT HOLE

STAND OFF POSTS (4)

VENT HOLE

TAP 10-32

KOVAR

VRE NO. 1

VRE NO. 2

KOVAR

1/32"

3/16"

1/4"

3/32"

2 7/16"

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using standard glass to Kovar vacuum feed throughs with extra length glass portions purchased from the Royal Glass Apparatus Company of Tulsa, Oklahoma.

Ion current readout. - The C^{13} isotope ratio difference, δ, between two samples of carbon is defined as:

$$\delta = \left(\frac{R_2}{R_1} - 1 \right) \times 1000$$

where
$$R = \frac{C^{13}}{C^{12}}$$

If a particular carbon sample is established as a standard ratio then all other samples can be measured relative to this standard and

$$R_1 = \frac{C^{13}}{C^{12}} \quad \text{ratio for the standard carbon sample}$$

$$R_2 = \frac{C^{13}}{C^{12}} \quad \text{ratio for the unknown carbon sample}$$

In a system utilizing carbon dioxide as a "working gas" the carbon isotope ratio is actually measured by comparing the concentration of oxidized C^{13} isotopes to oxidized C^{12} isotopes. With the dual ion collector described above the measured ratio is given by:

$$R = \frac{\text{number of mass 45 ions collected}}{\text{number of mass 44 ions collected} + \text{number of mass 46 ions collected}}$$

Both mass 44 and 46 appear in the denominator because they both must strike collector 2 (Figs. 1 and 18) when mass 45 is focussed on collector 1. In terms of the isotopic variations of carbon dioxide present as ions striking the collectors this ratio is given by:

$$R = \frac{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16} + C^{13}O^{16}O^{17} + C^{12}O^{16}O^{18}}$$

and for simplification can be expressed as

$$R = \frac{a}{b}$$

where

$$a = \text{ions falling on collector 1}$$

$$b = \text{ions falling on collector 2}$$

Substituting these symbols into the expression for δ one obtains

$$\delta = (\frac{a_2/b_2}{a_1/b_1} -1) \times 1000$$

If oxygen isotope ratios of the standard and the sample are identical and the denominators b_1 and b_2 are made equal during the measurements of the standard and sample gas ratios, the expression for δ reduces to:

$$\delta = (\frac{a_2}{a_1} -1) \times 1000$$

Note:

The above expression is not strictly true because of the uncertainty of the contribution of the $C^{13}O^{16}O^{17}$ to $\underline{b}$ and the related uncertainty of the contribution of the $C^{12}O^{16}O^{17}$ ion to $\underline{a}$. If no C^{13} species were present in the denominator, matching b_1 to b_2 would also match the contribution of the $C^{12}O^{16}O^{17}$ ion to a_1 and a_2 and δ would be exactly defined. The maximum uncertainty due to this factor can be determined from the constant oxygen isotope ratios and the range of C^{13} ratios known to occur and is found to be less than 0.1 parts per million. This error is of no consequence since the overall instrument designs limits precision to ± 20 parts per million.

The ion current readout system must, therefore, be capable of performing two primary functions: (1) to

provide a means of balancing the collector 2 ion currents with high precision and (2) to provide an accurate and highly precise means of determining the relative values of the ion currents collected on collector 1 for the standard sample gas.

The ion current readout system is shown in the block diagram of Fig. 1 and schematically in Fig. 19. This part of the system is unique to isotope ratio difference mass spectrometers. Two identical vibrating reed electrometers (Cary Model 401), a Kelvin-Varley Decade Divider (General Radio Model 1454-AH), a buckout-error circuit for electrometer no. 2, and a recorder selector switch constitute the entire readout system when connected as shown.

Only electrometer no. 2 and the buckout-error circuit are used to balance the ion currents falling on collector 2 from the standard and sample gases. The electronic current produced by the ion beam striking the collector is fed to electrometer no. 2 which produces a 0-30 volt proportional signal across its output voltage divider. The switch shown to the left of meter M1 diverts this output signal to the center zero 50 mA meter M1. An equal but opposite polarity signal is applied to the other side of M1 by closing switch S1 and adjusting potentiometer R14 to give a zero reading on M1. Switch S2 is used to vary the meter range so that the circuit may be balanced with a greater precision using the higher sensitivities. When balanced on the 0.1 volt range this circuit is capable of indicating changes in electrometer output of ± 1 mV. Typical operating parameters produce an 18 volt output signal on electrometer no. 2 so that it is possible to match the signals produced by the standard and sample gas within one part in 9000.

When the standard and sample ion currents are matched for collector 2 ($b_1 = b_2$) the buckout-error circuit is turned off and the recorder selector switch S3 is placed in the BAL position to determine the relative intensities of the ion beam collected by collector 1 for the standard and sample gas. The output signal from electrometer no. 2 is now tapped off at the one volt level on the electrometer divider and fed to the input J1 of the decade attenuator. (Note that the ion beam containing nearly all

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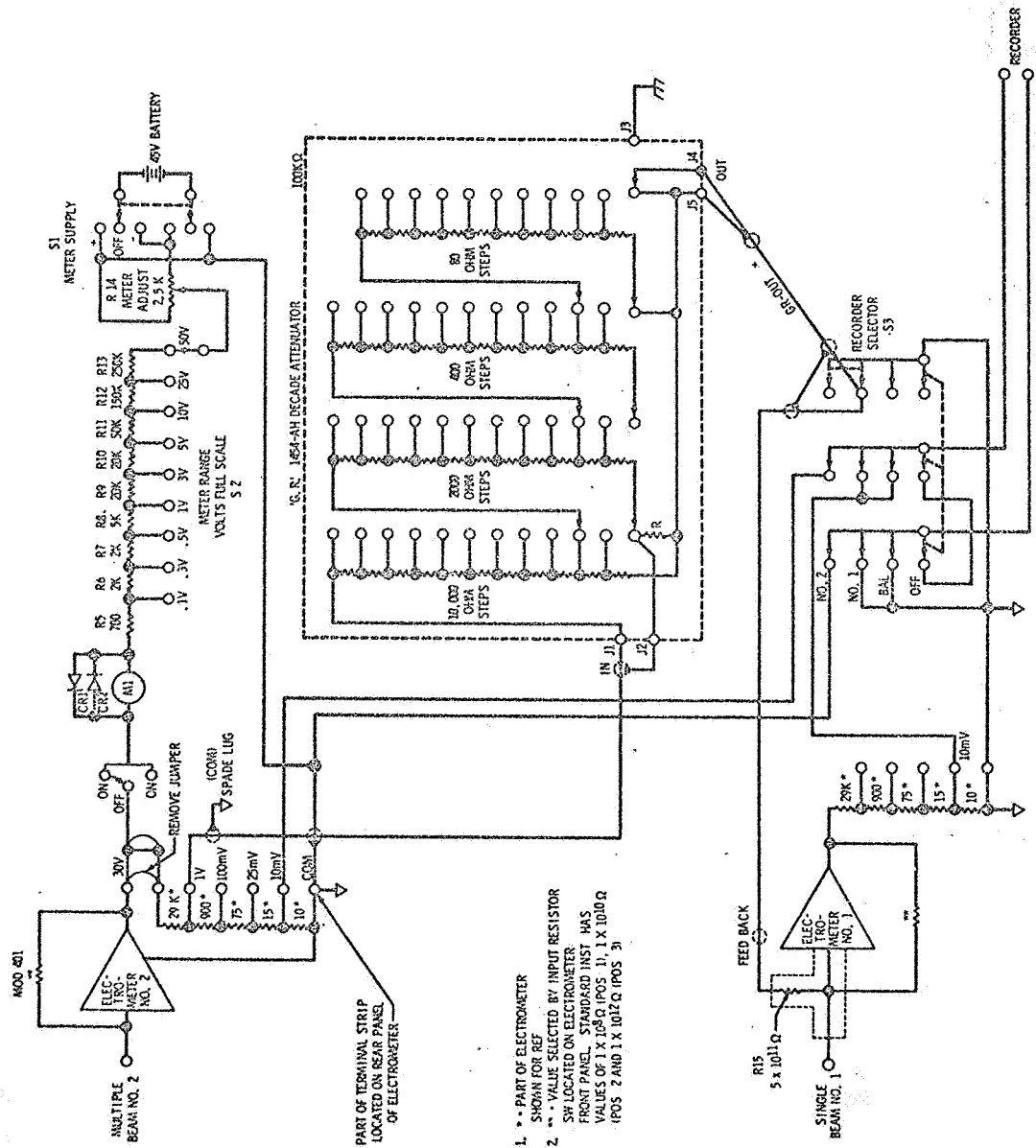
the major isotope is fed to electrometer no. 2). The
decade attenuator serves as a simple voltage divider with
one end receiving the "high" voltage signal and the other
end going to ground and the center tap output J4. The
decade attenuator output is connected via S3 to the feed-
back resistor R15 at the input to electrometer no. 1.
Electrometer no. 1 thus has two inputs: one from collec-
tor 1 and the other of opposite polarity through R15 from
the attenuator. If these two signals are exactly bal-
anced they will cancel each other and cause the output
of electrometer no. 1 to read exactly zero when the range
switch is on the 0.3V. The decade attenuator setting
required to balance or null these two signals is, there-
fore, directly proportional to the ion beam collected by
collector 1 (previously designated a), or mathematically:

$$a = kA$$

where k is a proportionality constant. This null method
requires that the zero drift characteristics of electro-
meter no. 1 be extremely good. The attenuator settings
(A_1 and A_2) required to balance these two inputs is deter-
mined for both the standard and sample gas, respectively,
and since the proportionality constant is identical can
be used to calculate δ as shown below:

$$a_1 = kA \qquad\qquad\qquad a_2 = kA_2$$

$$\delta = (\frac{kA_2}{kA_1} - 1) \times 1000$$

$$\delta = (\frac{A_2}{A_1} - 1) \times 1000$$

There are several factors causing k to deviate from unity
and to be so unpredictable that actual intensities cannot
be determined. These include divider linearty, indeter-
minate divider attenuation, feedback resistor value,
whether the measurement is actually made at a null posi-
tion, ion transmission and collection efficiencies,
contact potentials, etc.

The ion current readout system can also be used as
an ion current monitor to measure the beam collected on

either collector.· This is accomplished by reading the outputs directly off the electrometer meters with the selector switch S3 in the OFF position. Either of these outputs can be recorded by placing selector switch S3 in the no. 1 or no. 2 positions. This mode is used in aligning and focusing the mass spectrometer. The buckout-error circuit can also be used to gain more precise alignment and focusing.

INSTRUMENTAL OPERATING PROCEDURES AND PARAMETERS

Sample Preparation System

Tank oxygen is first purified by passing it over copper oxide heated to $700^{\circ}C$. The copper oxide used in both furnaces of the sample preparation subsystem was prepared by oxidizing electrolytic copper using the same tank of oxygen subsequently used for combusting samples. Each furnace contains approximately 25 g of the copper oxide. The furnace effluent is passed through the liquid nitrogen cooled trap T1 to remove any condensable impurities. The purified oxygen is then stored and measured in the oxygen storage bulb and connecting lines.

A weighed solid sample is placed in a prefired alundum combustion boat and placed in the loading tube just outside the combustion furnace. Enough sample is used to produce approximately two standard cubic centimeters of carbon dioxide. A cover is placed over the standard taper joint using slight heat and only enough Apiezon N grease to cover about one-half the length of the ground portion of the joint after vacuum is achieved. A magnetic push-rod is loaded into the joint cover as it is put into position. If an excessive amount of grease is used it will be drawn through the joint under vacuum and may contaminate the push-rod. Care must also be taken not to touch the push-rod, sample boat or inner surfaces of the combustion tube when loading the sample; and all grease must be carefully cleaned from the loading inlet cover when removing the sample. This is done by using tongs and a good laboratory tissue such as Kimwipes for grease removal. Slight heating greatly facilitates

grease removal. Solvents cannot be used as they invariably end up in the furnace as a contaminant. The furnace and combustion train are then pumped to a vacuum of less than one micron to remove atmospheric pressure.

In addition to the copper oxide the combustion furnace also contains about five grams of fine silver wool. The silver wool is placed in a portion of the furnace which maintains a temperature of $500-600^{\circ}C$ when the sample combustion portion is at $900-950^{\circ}C$. The silver wool removes any sulfur present by converting it to the sulfate which will decompose at $635^{\circ}C$ (8). The brown black oxide of manganese, Mn_2O_3, will also serve this purpose, but is more difficult to obtain and handle. The removal of sulfur in some manner is essential since it forms sulfur dioxide and sulfuric acid which are corrosive and make high precision mass spectrometric isotope ratio measurements nearly impossible.

Upon achieving a good vacuum the combustion train is valved off and filled to approximately 20 cc of oxygen which is a factor of ten excess for two standard cubic centimeters of product carbon dioxide. Since the vapor pressure of oxygen is only 15 cm at liquid nitrogen temperature ($-196^{\circ}C$), this may require handling liquid oxygen in trap T1. The required amount of oxygen is previously stored in the storage volume by warming T1 and in our specific case, letting the liquid oxygen evaporate until the pressure is obtained. It was shown that no condensable gases are carried over by this procedure. The main combustion furnace is heated to $950^{\circ}C$ and the Toepler pump is actuated to cycle the gas. The sample is then thrown into the furnace using a magnet and the magnetic push-rod and the push-rod is withdrawn. Liquid nitrogen is placed on trap T2 to condense the carbon dioxide as it is produced. Carbon monoxide has an appreciable vapor pressure at $-196^{\circ}C$ and is recirculated until completely oxidized. Upon completion of combustion the trap T2 is isolated from the furnace and excess oxygen pumped away. The carbon dioxide is distilled from the trap using a dry ice-methoxy propanol bath, frozen into the cold finger, measured by the manometer, and transferred to the carbon dioxide removal bulb. When burning difficulty combustible samples such as carbonaceous chondrite meteorites, it is wise to check for complete

combustion by cycling the gas through the train with liquid nitrogen on T2 to see if additional carbon dioxide is trapped out. Combustion time for samples will vary from 30 minutes to two hours depending on their nature and is difficult to predict for geochemical samples.

The furnace heater is turned off and the furnace cooled to room temperature before opening to load the next sample. This and the production of the copper oxide from copper foil and tank oxygen eliminate oxygen exchange between the copper oxide and atmospheric oxygen and eliminates the uncertainty in results due to this exchange as described by Craig (9). The sample preparation time using this method is approximately 75 min plus combustion time, 15 min to load the sample and pump out the furnace, 30 min to heat the furnace, and 30 min to cool the furnace. The product carbon dioxide is isolated and placed in the bulb while the furnace is cooling.

The sample combustion procedure using the alternate sample preparation subsystem is as follows. With the heated furnace lowered the combustion tube is removed by breaking the O-ring seal while maintaining vacuum in the remainder of the system. The sample is loaded into the sample holder and placed into the tube taking care not to touch any of the interior portion with bare fingers. Laboratory tissues or tongs can be used to accomplish this. The tube is then sealed to the vacuum system by clamping the O-ring seal and the atmospheric gases removed through the rough and high vacuum lines until the pressure is below 25 microns. Oxygen is then admitted to the furnace to a pressure of 35 cm. The tube is then isolated by closing the stopcock above it and the hot furnace raised to begin heating the sample. After 10 min has elapsed liquid nitrogen is placed on the cold finger to condense the product carbon dioxide. The finger is left warm for first 10 min to prevent condensing any products of incomplete combustion such as alcohols or ketones. The sample is then burned for an additional 10-20 min. Tests for completeness of combustion given in Table 2 show that no type of sample requires more than 30 min total combustion time in this furnace. The furnace is lowered and the tube cooled to ambient with a small blower. A dry ice-solvent bath is placed on the U-trap and a liquid nitrogen bath on the second cold finger. The liquid nitrogen is removed

TABLE 2

TIME REQUIRED FOR COMPLETE COMBUSTION

Sample Type	Initial Combustion Time	Additional CO_2 produced for double the initial combustion time
Carbonaceous Chondrite	60 min	$< 5 \times 10^{-3}$ torr
" "	50 min	$< 5 \times 10^{-3}$ torr
" "	40 min	$< 5 \times 10^{-3}$ torr
" "	30 min	$< 5 \times 10^{-3}$ torr
" "	15 min	40×10^{-3} torr
Oxalic Acid	30 min	$< 5 \times 10^{-3}$ torr
" "	15 min	$< 5 \times 10^{-3}$ torr
Petroleum	30 min	$< 5 \times 10^{-3}$ torr
"	15 min	12×10^{-3} torr
Graphite	30 min	$< 5 \times 10^{-3}$ torr
"	15 min	$< 5 \times 10^{-3}$ torr

from the first cold finger allowing the product carbon
dioxide to evaporate. A pressure minimum on thermocouple
gauge no. 1 indicates the completeness of carbon dioxide
evaporation and the start of evolution of water vapor
from the first cold finger. Shortly thereafter the
pressure reading on thermocouple gauge no. 2 reaches less
than one micron. At this time the stopcock in front of
the second cold finger is closed thereby isolating the
product carbon dioxide. Cold finger no. 2 is then warmed
and the carbon dioxide pressure measured by manometer no.
2. During this warming the furnace stopcock can be closed,
a new sample loaded into combustion tube, the U-trap
cleaned; and the combustion tube pumped out, recharged,
and the next run started. After the carbon dioxide
pressure is measured it is transferred to a collection
bulb for subsequent ratio determination.

The alternate sample preparation technique has
proved to have several advantages over the older Craig-
type procedure. The complete sample preparation proce-
dure requires only 40 mins. The combustion tube is easily
accessible for routine inspection or cleaning and can be
easily replaced. The sample can be observed during vacuum
pump down. There is no need for a Toepler pump to cycle
the combustion gases because of the much smaller volume
involved. The vacuum system requires fewer components
and is considerably less expensive than the older type.
The foremost advantage, however, is the simplicity of
operation which allows relatively inexperienced operating
personnel to achieve highly reproducible results in a
short time.

Sample Inlet System

The carbon dioxide "working gas" is placed in the
working volume above the mercury pistons on the high
pressure side of the capillary leaks by freezing into the
cold fingers. The capillary leaks control and reduce the
gas flow to a value which will limit the ion source press-
ure to values below its maximum operating pressure of 10^{-4}
torr without fractionating the gas. The working volume
(about 10 ml) and pressure (3-5 cm) above the leaks is
such that the flow through the leaks is essentially con-
stant with time during the ratio measurement on the mass

spectrometer. The measured flow at 3 cm pressure was 5×10^{-10} moles/sec for these leaks. The mercury pistons are adjusted so that mass 44 beam intensity is identical for both sample and standard and does not fluctuate during switching. This is done by actuating the switching valve to direct first standard and then unknown sample gas into the ion source and noting the beam intensity on the multiple beam electrometer. The buckout circuit described earlier is used for this balancing operation in high precision work. In all cases both gases experience the same flow and pressure conditions. This is accomplished by reproducing the source pathway with a waste gas pathway. Both pathways terminate in the same ion pump. When the sample and standard beam intensities are equal no related correction is needed in reducing the mass spectrometer data (9). Upon achieving equal flow of standard and sample gas, ratio recording can begin.

Mass Spectrometer

The first step in making the actual ratio measurement on the mass spectrometer once the standard and sample gas flows are balanced, is the alignment of the ion beam. The standard gas is directed into the ion source for the alignment. The accelerating voltage is set at 4414 (center of the 45 peak) volts so the mass 45 beam is centered in the center cup of the dual collector. The extraction, deflection, and focus voltages are adjusted to give a maximum mass 45 beam reading on the electrometer. The readout system is then placed in the ratio recording mode with the voltage divider set to pen a null reading and the accelerating voltage readjusted to the position where a one volt change causes the least change in the null position. This final adjustment has been found to be the most satisfactory in establishing instrument parameters to give the most reproducible ratio measurements. Experience has shown that after an initial warm-up period of one hour only the extraction voltage requires any further adjustment from sample to sample. This, of course, speaks well for the design and construction of the instrument.

When the mass spectrometer is properly aligned the null position is determined by making a trace on the

recorder for approximately two min. The sensitivity of
the readout is calibrated by changing the voltage divider
setting by a few parts per thousand and recording the
deflection. The gas switching valve is then actuated to
direct sample gas into the ion source with the recorder
continuously tracing. The voltage divider setting is
quickly adjusted to return the recorder pen as close as
possible to the trace position for the standard gas. The
switching valve is actuated in approximately two mins to
again direct standard gas into the ion source. The switch-
ing between standard and sample is repeated three times
ending with standard gas in the ion source. The voltage
divider is then returned to the original setting again
causing a deflection in the recorder trace which provides
a second determination of the readout sensitivity. The
readout sensitivity is directly proportional to the flow
through the leaks. The flow actually changes slightly
over a 10 min period due to decreasing pressure in the
working volume above the mercury pistons as the gas is
pumped away. This error is averaged out in the readout
sensitivity calibration procedure described above.

There are several other operating parameters which
should be observed to obtain the best precision possible
in ratio measurements. The standard gas should have a
C^{13} content within 1% or 10 parts per mil (10o/oo) of the
sample gas. Larger differences require the use of addi-
tional banks of resistors in the divider network which
contribute additional error. Several standards must be
kept and the standard gas changed when an initial com-
parison shows a difference greater than 10o/oo. The
sensitivity of the readout system should be high, pref-
erably better than 0.25o/oo per recorder chart division.
Since recorder chart deflection cannot be determined to
better than ±0.1 chart division this can be the major
factor in readout precision. This sensitivity is directly
related to ion beam current and is a function of the ion
source efficiency, the amount of gas flowing through the
capillary leaks, and the electrometer range setting. The
efficiency of the ion source used in this study was deter-
mined and found to be equal to that for commercial in-
struments. A good ion source efficiency is especially
important when working with small samples as in this study.
A third factor that is important is maintaining low random
noise levels. The recorder traces shown in the next

section illustrate this factor. When the noise level is less than ±3-4 mV the line representing the true trace is fairly easy to determine to ±0.1 chart division. If the noise level is on the order of ±7-10 mV it is difficult to determine the true trace to better than ±0.5 chart division. The noise level increases for lower ranges on the electrometer as the sensitivity increases and these factors must be balanced for the particular instrument. The noise level was minimized by using good shielding, careful soldering, and taking great care to keep the collector feed-throughs clean at all times. High voltage leakage or arcing in the ion source is also a source of noise and is minimized by bakeout. Bakeout cleaning of the capillary also minimizes noise by stabilizing the gas flow. Typical operating conditions for the instrument are given in Table 3.
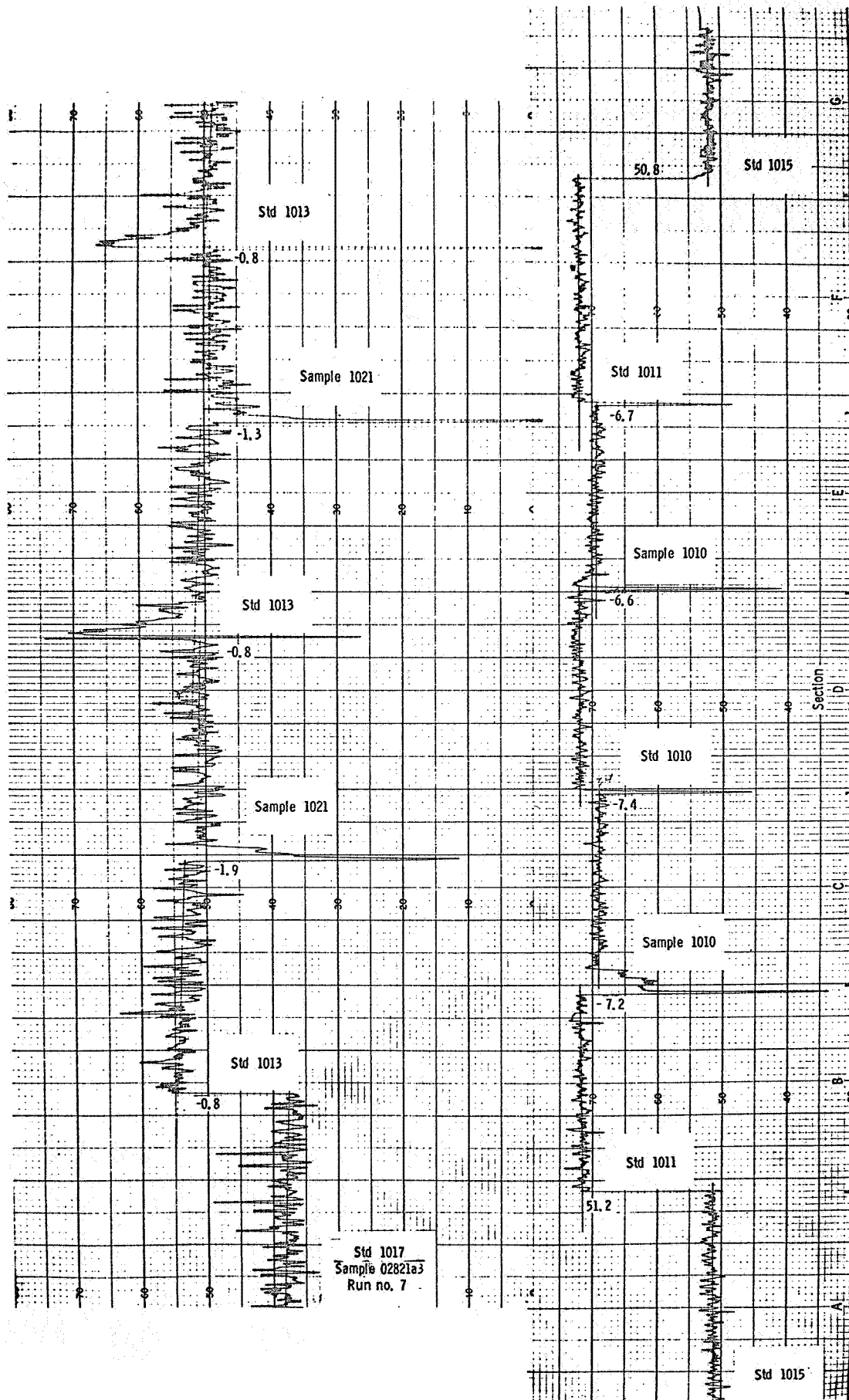
DATA HANDLING

A sample of a recorder chart tracing obtained from the ratio recording procedure under typical operating conditions is shown on the right in Fig. 20. Section A of the tracing represents the initial null position with standard gas directed into the ion source. Any departure of the tracing from a straight line is attributed to random noise pulses either generated within the electronic components or contributed by external disturbances. The true null position is therefore determined by drawing a line which bisects or averages these noise pulses. It was found that this can be done most reproducibly by using a clear plastic straight edge and drawing the "average" line so that about the same amount of tracing appears on either side. The random noise in this case is approximately ±3 mV and the "average" line is easy to locate. Fig. 20 also shows a recorder chart tracing on the left with random noise of approximately ±10 mV. It is evident that locating the "average" line is much more imprecise in this case.

Section B of the right tracing indicates the deflection caused by changing the voltage divider setting to calibrate the read-out sensitivity. Subsequent sections (CD&E) of this tracing record the null position as stand-

TABLE 3

TYPICAL OPERATING PARAMETERS FOR THE MASS SPECTROMETER

Accelerating voltage	4412 volts
Extraction voltage	10 volts
Filament current	4.0 amps
Filament emission (trap current)	120 microamps
Electron energy	66 volts
Gas flow	5.0×10^{-10} moles/sec
Mass 44 + 46 beam current	1.8×10^{-9} amps
Mass 45 beam current	1.4×10^{-11} amps
Electrometer #1 range	300 mv
Electrometer #1 input resistor	10^{12} ohms
Electrometer #2 input resistor	10^{10} ohms
Recorder range	10 mv
Recorder chart speed	1 in/min
Electrometer #1 Feedback Resistor	5×10^{-11} ohms

Std 1015

50.8

Std 1013

-0.8

Std 1011

-6.7

Sample 1021

-1.3

Std 1013

Sample 1010

-6.6

Std 1013

-0.8

Std 1010

Section D

-7.4

Sample 1021

-1.9

Sample 1010

-7.2

Std 1013

-0.8

Std 1011

51.2

Std 1017
Sample 02821a3
Run no. 7

Std 1015

ard and sample gas are alternately directed into the ion source as indicated by the markings on the chart. The numbers refer to the settings on the voltage divider. The final two sections (F&G) of the tracing are the second sensitivity calibration described previously. Average lines are drawn through each portion of the tracing and their separation measured by a scale. The readout sensitivity can then be calculated as below:

C.D. = average chart deflection taken from tracing

R_1 = initial voltage divider setting

R_2 = new voltage divider setting

$$\text{Sensitivity (S)} = \frac{R_1 - R_2}{R_2} \times \frac{10^3}{C.D.}$$

This factor is used to correct the ratio calculated from the voltage divider settings when the sample and standard null positions are not identical. The measured ratio difference between the sample and standard can be determined from this data since the system is designed and operated so that all factors are fixed except C^{13} content in the sample and is calculated as follows:

R_s = null voltage divider setting for standard gas

R_u = "   "   "   "   " sample gas

D = difference in standard and sample null positions from tracing

$$\text{Raw Ratio (RR)} = \left[\left(\frac{R_u - R_s}{R_s} \times 10^3 \right) \right] \pm DS$$

The sign of the first term is dependent on the relative C^{13} contents and is negative if the sample contains less C^{13} than the standard. The sign of the second term is determined by noting the relative positions of the standard and sample null positions and keeping in mind the fundamental principles of the ratio readout circuitry. This is best illustrated by an example. If the standard is nulled at a voltage divider setting of 1000, this means that 10% of the current developed in the readout circuit by the major isotope ion beam is required to buckout the minor isotope or C^{13} signal. If

a sample gas is nulled at an identical position with a
voltage divider setting of 1010 then a large fraction of
the major isotope signal is required to buckout the C^{13}
signal. Since the sample and standard major beam inten-
sities have previously been matched the C^{13} content of
the sample is greater than the standard. If the sample
null position does not coincide with the standard and
is to the right of the standard, then the minor isotope
has been overcompensated and the correction should have
a negative sign. Alternately, if the sample null position
is to the left of the standard, the minor isotope is
undercompensated and the correction should have a positive
sign. Note that the zero position for the chart presented
is on the right.

Craig (9) has described two instrumental correction
factors for mass spectrometric isotope ratio measurements
of carbon dioxide which may be applied to the measured
ratio: (a) a correction for mixture of the sample and
standard gas in the ion source due to improper closure of
the switching values and (b) a correction arising from
a contribution (tailing) of the mass 44 beam to the mass
45 and 46 beams. Neither of the corrections are applicable
to the values measured with the instrument described here
since there is no measurable leak in the values and the
resolution is sufficient to eliminate tailing. Craig
has also considered correction factors based on the
variation of oxygen isotope ratio differences between
the standard and sample gases. These variations in oxygen
isotope variations were caused by oxygen exchange between
the CuO catalyst, the tank oxygen, and air oxygen. In
this study any such exchange was eliminated by preparing
the CuO by oxidation of pure copper with tank oxygen,
using this same tank of oxygen for all combustions,
cooling the CuO before opening the furnace to atmosphere,
and pumping out all atmospheric oxygen prior to charging
the furnace with tank oxygen. Proper design and opera-
tion of the measurement system has resulted in measured
ratios which require no corrections. Measured ratios
can be converted to values relative to PDB for the sample
if values for the standard relative to PDB are known.

ACCURACY OF RATIO MEASUREMENTS

The closeness of approach of a number of similar or replicate results to a common value in a series of measurements is defined as the precision or reproducibility. Errors which contribute to the lack of precision can be broadly classified into two categories: (a) determinate or systematic errors, and (b) indeterminate or random errors. In the measurement of isotope ratios as described here random errors are due to the statistical flucations in the mass spectrometer ion source and electronic readout system and systematic errors are largely a result of the sample preparation technique. In order to isolate these two contributions reproducibility data was obtained for the gas analysis subsystem by making repetitive measurements on samples of purified carbon dioxide gas. The standard gas in this gas was 99.8% purity "bone dry" grade carbon dioxide purchased in a lecture bottle and further purified by fractional distillation. In this way any errors contributing to lack of precision were limited strictly to instrumental operating characteristics, and instrumental operating parameters discussed above, were adjusted to give maximum precision. The ultimate precision achieved is shown in the data of Table 4.

After establishing the gas analysis subsystem reproducibility, data on the analysis of typical standards was collected. This data served as a means of evaluating sample preparation techniques since any loss of precision over samples not requiring such preparation must be attributable to systematic errors in sample preparation. This technique was used to develop the sample preparation techniques described in above. Precision obtained for the Craig-type sample preparation procedures are given in Table 5. The standards were selected to provide incremental values of approximately 10o/oo so that in subsequent analyses the measured raw ratios would not be larger than 10o/oo. Samples of high purity graphite and vacuum pump oil were burned to obtain much of the data used in evaluating sample preparation procedures. Later, data was obtained for establishing precision and accuracy of the ratio determinations from NBS standards of oil and oxalic acid. It is obvious that some problem existed during use of the Craig method. There was later found to

TABLE 4

PRECISION OF CARBON DIOXIDE RATIO MEASUREMENTS

Sample	Measured δC^{13} (o/oo)*	Avg. $\pm$ Std. Dev. (o/oo)
A	+12.16	
A	+12.21	
A	+12.28	
A		+12.21 $\pm$ 0.06
C	+14.33	
C	+14.30	
C	+14.26	
C	+14.28	
C	+14.27	
C	+14.20	
		+14.27 $\pm$ 0.05

*δC^{13} relative to a gas of unknown isotopic composition placed in the standard side of the capillary inlet leaks.

TABLE 5

EVALUATION OF CRAIG-TYPE SAMPLE COMBUSTION TECHNIQUES

Date	Sample	Measured δC^{13} (o/oo)*	Avg. $\pm$ Std. Dev.
7/4/68	Pump Oil	+13.23	
7/8/68	Pump Oil	+14.04	
7/11/68	Pump Oil	+14.06	
7/15/68	Pump Oil	+14.07	
7/23/68	Pump Oil	+13.69	
			13.82 $\pm$ 0.35
7/9/68	Graphite	+18.60	
7/9/68	Graphite	+19.36	
7/11/68	Graphite	+19.35	
7/13/68	Graphite	+20.13	
			19.36 $\pm$ 0.65

*δC^{13} relative to a gas of unknown isotopic composition placed in the standard side of the capillary inlet leaks.

be a leak in the furnace combustion tube which may have
contributed to this imprecision. Results for the alternate
method are given in Table 6 and have better precision
than those of Table 4. This probably is due to the
additional experience of the mass spectrometer operator.
It is also apparent that the sample preparation procedure
developed in this laboratory does not affect the precision
of the ratio measurements. The differences in precision
for the oxalic acid, graphite and oil could be due to
two factors. The graphite is not as pure or homogeneous
as the oxalic acid and sulfur is present in the oil but
not in the oxalic acid or graphite.

The NBS standard oxalic acid and oil were also used
to establish the accuracy of the ratio measurement system
since they have known δC^{13} values. This was done by
using the oxalic acid carbon dioxide as the standard gas
and calculating a δC^{13} value for the oil from the measured
ratio data. A third standard was established by measuring
the ratio difference between the NBS oil and the purified
carbon dioxide from the lecture bottle. The accepted
δC^{13} value for the oxalic acid is $-19.35 \pm 0.05\%$ vs PDB
and for the NBS oil the value is $-29.40 \pm 0.05\%$ vs PDB.
The data obtained in this study is tabulated in Table 7.
The δC^{13} values are calculated by adding or subtracting
the measured ratio to/from the standard δC^{13} value as
the sign indicates. The measured δC^{13} value for the oil
is within the error of the accepted value indicating
the accuracy of the system is as good as the precision.

The above results show that the instrumentation and
operating techniques developed during this study are
capable of producing the high precision ratio measure-
ments necessary for the study of meteoritic organic matter.

CONCLUSIONS

The scientific accomplishments of this research
effort up to the time of this report involve three distinct
areas of investigation. The first area involved the
evaluation of all experimental equipment and techniques
in order to verify the validity of the procedures and
establish values for complete system reproducibility. The

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TABLE 6

EVALUATION OF ALTERNATE SAMPLE COMBUSTION TECHNIQUE

Date	Sample	Measured δC^{13} (o/oo)	Avg. $\pm$ Std. Dev.
8/5/68	NBS Oxalic Acid[1]	21.61[3]	
8/5/68	NBS Oxalic Acid[1]	21.66[3]	
8/5/68	NBS Oxalic Acid[1]	21.56[3]	
			21.61 $\pm$ 0.05
8/15/68	Graphite	-21.59[3]	
8/15/68	Graphite	-21.46[3]	
8/15/68	Graphite	-21.47[3]	
			-21.51 $\pm$ 0.07
8/6/68	Oil NBS-22[2]	-10.22[4]	
8/7/68	Oil NBS-22[2]	-10.08[4]	
8/9/68	Oil NBS-22[2]	-10.08[4]	
8/15/68	Oil NBS-22[2]	-10.02[4]	
8/22/68	Oil NBS-22[2]	-10.11[4]	
9/6/68	Oil NBS-22[2]	- 9.97[4]	
			-10.08 $\pm$ 0.08

1. δC^{13} value of NBS-22 is -29.40 o/oo vs PDB
2. δC^{13} value of NBS oxalic acid is -19.35 o/oo vs PDB
3. δC^{13} relative to a gas of unknown isotopic composition placed in the standard side of the capillary inlet leaks.
4. δC^{13} relative to the CO_2 combusted from the NBS oxalic acid placed in the standard side of the capillary inlet leaks. The actual value from 1 and should be 10.05.

TABLE 7

ACCURACY OF RATIO MEASUREMENTS

Sample	Standard*	Measured δC^{13} (o/oo)	δC^{13} (o/oo vs PDB)
NBS Oil	NBS Oxalic Acid	-10.22	-29.57
NBS Oil	NBS Oxalic Acid	-10.08	-29.43
NBS Oil	NBS Oxalic Acid	-10.08	-29.43
NBS Oil	NBS Oxalic Acid	-10.02	-29.37
NBS Oil	NBS Oxalic Acid	-10.11	-29.46
NBS Oil	NBS Oxalic Acid	- 9.91	-29.26

*δC^{13} value for NBS oxalic acid is -19.35% vs PDB.

Average δC^{13} measured = -29.43 ± 0.08 Standard Deviation.

Accepted δC^{13} = -29.40 ± 0.05 Standard Deviation.

second area consisted of a study of the carbon isotope
ratios of some organic geochemical samples thought to be
primordial. The final effort discussed in this report is
the investigation of the carbon isotope ratios of organic
material found in meteorites. The results for the first
two areas are complete, but data is still being accumulated
on the meteorites and only preliminary results are given.
A supplement to this report will include the final results
of the meteorite studies.

Organic Geochemical Samples

Stable carbon isotope, gas chromatograph and mass
spectral analyses were obtained and compared with other
data on organic geochemical samples thought to be
primordial. The specimens were obtained from inclusions
in hydrothermal mineral deposits of the Derbyshire,
England area. Previous geological, chemical, and physical
data suggested a possible abiogenic or prebiogenic ex-
planation of the origin and nature of this material. The
carbon isotopic composition of the Derbyshire material is
given in Table 8. The δC^{13} values for natural petroleum
fall in the range -2 o/oo to -35 o/oo.

TABLE 8

CARBON ISOTOPE DATA ON DERBYSHIRE SAMPLES

Sample	δC^{13} measured (o/oo vs PDB) Univ. of Houston	Woods Hole	Commercial
Carbonite	-29.7	-29.6	-29.9
Olefinite	-29.5	-29.8	-28.6
Foxite	-25.6	-29.7	-28.8
Vaseline	-30.4	-31.0	-30.7

The values given in the second column were obtained
in our laboratory, those in the third column by the
Woods Hole Oceanographic Laboratory and the fourth column
by an outside commercial laboratory as a check. This
isotopic data along with hydrocarbon molecular composition
data indicate a marked similarity between the Derbyshire

material and ordinary petroleum, thus implying a
biological origin.

Meteorite Samples

Samples of the Orgueil, Mokoia, and Murray meteorites
are being studied in detail. These represent the Type I,
II and III classifications of carbonaceous chondrites.
The most significant feature of results obtained to date
is the serious effects on carbon isotope ratio measurements
that may be produced when carbonate is present in the
meteorite as exhibited by the data presented in Table 9.
The unground sample was burned with no treatment and con-
sisted of coarse sized particles on the order of 0.2 to 1
mm in diameter. The ground meteorite was homogenized in
a Spex Mixer/Mill for three minutes using a ceramic con-
tainer and ceramic grinding balls. It appears there is
a gross inhomogeneity in the meteorite. It is believed
this inhomogeneity is due to the presence of carbonate in
the meteorite which has previously been reported by
Dufresne (10), Clayton (11), has previously reported a
δC^{13} value of 59.4 o/oo for Orgueil carbonate. A similar
value of 61.4o/oo was measured in our laboratory by a
phosphoric acid treatment of the meteorite. The amount.
of carbon dioxide produced indicates the meteorite con-
tains approximately 0.3% carbonate carbon by weight. This
inorganic carbonate carbon would not be expected to be
homogeneously distributed throughout the meteorite since
it likely forms locally as an alteration product. The
total carbon present in Orgueil is on the order of three
percent and according to our results has a δC^{13} value of
-11.77o/oo vs PDB. Any value of δC^{13} measured without
removing the inorganic carbonate or adequately homogenizing
the meteorite may then vary considerably depending on the
carbonate content of the meteorite portion actually
measured.

TABLE 9

TOTAL CARBON ISOTOPE RATIO DATA FOR THE ORGUEIL METEORITE

Sample	δC^{13} (o/oo vs PDB)	Average
Unground 1	−8.55	
Unground 2	−12.02	
		−10.28 ± 2.5
Ground 1	−11.96	
Ground 2	−11.71	
Ground 3	−11.65	
		−11.77 ± 0.16

References

1. Boato, G.: Geochim. Cosmochim. Acta $\underline{6}$, 209-220, 1954.

2. Hayes, J.M.: Organic Constituents of Meteorites, NASA Report EFINS 66-118, 29-32, 1966.

3. Neir, A.O.: Rev. Sci. Instrum. $\underline{18}$, 398-411, 1947.

4. McKinney, C.R.; McCrea, J.M.; Epstein, S.; Allen, H.A.; and Urey, H.C.: Rev. Sci. Instrum. $\underline{21}$, 724-730, 1950.

5. Wanless, R.K.; and Thode, H.G.: J. Sci. Instrum. $\underline{30}$, 395-398, 1953.

6. Neir, A.O.; Eckelmann, W.R.; and Lupton, R.A.: Anal. Chem. 34:1358-1360, 1962.

7. Craig, H.: Geochim. Cosmochim. Acta $\underline{3}$, 53, 1953.

8. Lange, A.N.: Handbook of Chemistry, Handbook Publishers, Inc., Sandusky, Ohio, 1956.

9. Craig, H.: Geochim. Cosmochim. Acta $\underline{12}$, 133-149, 1957.

10. Dufresne, E.R.; and Anders, E.: Geochim. Cosmochim. Acta $\underline{26}$, 1085, 1962.

11. Clayton, R.N.: Science $\underline{140}$, 192, 1963.