

(4) Distance between the flange and the two focal surfaces for objects at infinity not located on the optical axis but subtending, with the latter, various angles with the iris closed. The difference between these two distances represents the amounts of pure astigmatism with which the lens is afflicted at that particular field angle; while the difference between each of these two measurements and the flange focal length as measured according to (1) represents the tangential and sagittal field curvature.

(5) Same as (4), but for different iris settings to determine the additional influence of coma and oblique spherical aberration.

It should be noted here again that the measurements (2) and (5) do not represent the mathematical image point for that particular aperture but rather the circle of least confusion, taking into consideration the sum total of all aberrations which come into play at the image formation for that particular point of the field.

The variations of these distances give a reliable measure for the evaluation of the lens performance under actual working conditions.

* Figure 2 shows the instrument mounted on a standard optical bench.

It is obvious that, from the standpoint of production engineering, the necessary computations have been reduced to an absolute minimum. Nearly all data required to plot graphs of the resolution of the lens at different apertures and field angles can be directly read off from the instrument.

The instrument is also very sturdy and needs no adjustment once it is set. Like the "microfocuser," it can be operated by an unskilled worker after very short instruction.

An instrument of this type has been in practical daily use for over a year and has given most satisfactory results.

Improvements in Mass Spectrometers for the Measurement of Small Differences in Isotope Abundance Ratios

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A Nier-type mass spectrometer and its associated electronic units have been constructed for the purpose of measuring small variations in the abundances of oxygen of mass 18 and of carbon of mass 13 in carbon dioxide, and of oxygen of mass 18 in oxygen gas, to an accuracy of ± 0.01 percent of the abundance of these isotopes.

The electronic units of the necessary stability for this degree of accuracy are described. A gas feed system is described which permits fast alternate introduction of the sample of gas to be analyzed and a standard gas into the mass spectrometer. All measurements of the variation in the abundance of the oxygen and carbon isotopes are made with reference to a standard.

DURING recent years great progress has been made in developing mass spectrometers for the measurement of the relative abundance of isotopes. Particularly sensitive instruments have been developed by Nier, Thode, and others.¹ Basically, the mass spectrometer and electronic units in our research were those described by Nier. We report only the changes we made in these that assisted us in being able to measure small differences in the abundance of the rarer isotopes in gaseous compounds. The method has been applied to carbon and oxygen in carbon dioxide and to oxygen in oxygen gas. Our success in securing this greater sensitivity depends both upon increasing the intensity of the ion beam and upon increasing the absolute sensitivity of detection. In doing this, it has been necessary to improve the stability

of the beam intensity and output from the amplifiers by the use of more stable power supplies, more reliable amplification systems, and an improved emission regulator. Also, it has been necessary to use a method for rapid change of samples in order to decrease errors due to general variability of the instrument with time, and it has proved essential that a recording potentiometer be used to detect and record the state of balance of the simultaneously collected ion beams. The instrument has been constructed with the objective of measuring small differences in isotopic abundances of the oxygen isotopes as a means of measuring paleotemperatures, but the instrument and our procedures may be useful in other researches.

POWER SUPPLY FOR ELECTROMAGNET

Figure 1 shows the circuit diagram of the power supply used to furnish the current for the magnet windings

¹ A. O. Nier, *Rev. Sci. Inst.* **18**, 398 (1947). Thode, Graham, Ziegler, *Can. J. Research* **B23**, 40 (1945). For an excellent review of this subject, see M. G. Inghram, *Advances in Electronics* **1**, 219 (1948).

and to supply some of the power requirements for the high voltage electronic unit.

Several measures are used to achieve good stability of the output of this power supply. The voltage to the screen of the 6L6 tubes (1V4 and 1V5) and the plate supply of the 12AU6 (1V13) amplifier tube is obtained from a separate power supply regulated by using OA2 (1V6 to 1V9) miniature voltage regulator tubes. A 5651 voltage regulator tube (1V11) is used to obtain a reference voltage. The ripple of the output is minimized by adjusting potentiometer 1P2. This potentiometer controls the balance of the bridge circuit operating through the isolating cathode follower tube (1V10) and the screen of the amplifier tube (1V13). The "H" network of which 1P2 is a part is designed so that the d.c. level of the output voltage is nearly independent of the setting of 1P2. This type of circuit is similar to the one described by McCrea and LeRoy.² Since the response of this circuit is rapid, the single condenser 1C3 provides ample smoothing of the input.

To further increase the stability of the power supply, the current for the heaters of the critical amplifier tubes (1V10, 1V12, and 1V13) is supplied by the output of the power supply itself. By using switch 1S3, the unit is allowed to warm up under reduced output voltage. Relay 1S2 protects the circuit from excessive voltage rise during operation. A properly adjusted power supply unit has an output of 250 volts and supplies a current of about 200 milliamperes. The ripple is 1.5 millivolts, peak to peak, with a noise level of about 0.6 millivolt. The internal resistance for direct current conditions is 0.35 ohm and for 60 cycle load variation about 0.6 ohm. A 1.1-volt (1 percent) variation in the alternating current input appears as a 0.000184 percent, or a 0.5 millivolt, variation in the output. The 115-volt power line is regulated by a Sola Constant Voltage Transformer.

The magnet current can be varied by varying the resistance in series with windings by means of controls 1P4 and 1P5 and switches 1S4 and 1S5. A Helipot 1P5, connected to a motor by a clutch mechanism, allows

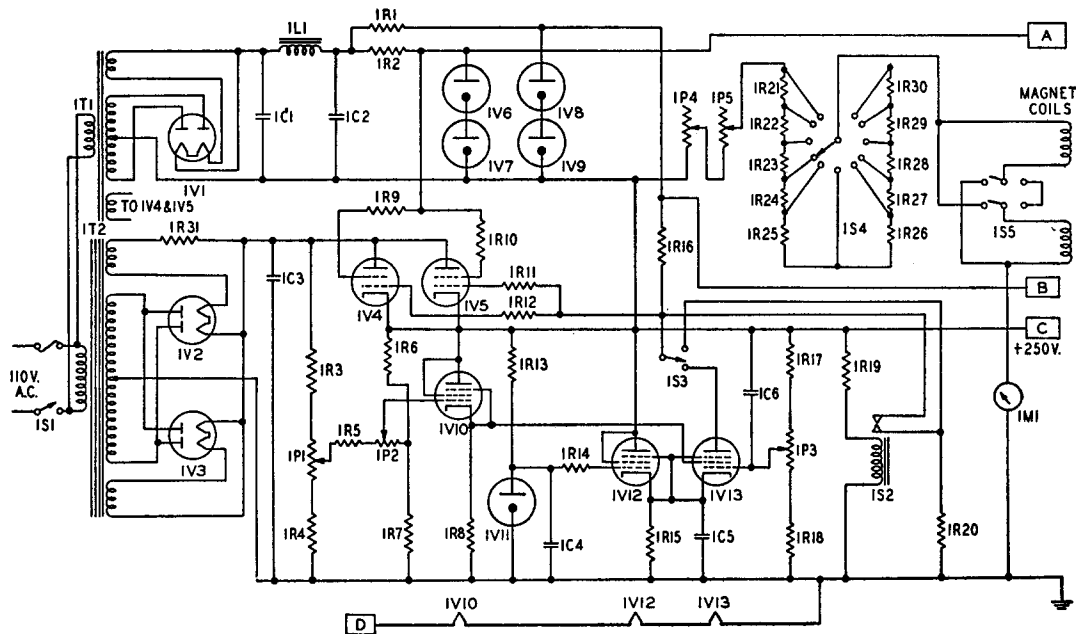


FIG. 1. Power supply (regulated).

1R1	13,500 ohms, 10 watt, wire wound	1C4, 1C5	0.01 mfd 400 v
1R2	5000 ohms, 10 watt, wire wound	1C6	250 micro-microfarad
1R3	68,000 ohms, 1 watt	1V1	5Y3
1R4	39,000 ohms, 1 watt	1V2, 1V3	5U4G
1R5	22 megohms, 1 watt	1V4, 1V5	6L6
1R6	50,000 ohms, precision wire wound	1V6, 1V7, 1V8, 1V9	OA2
1R7	75,000 ohms, precision wire wound	1V10, 1V12, 1V13	12AU6
1R8	35,000 ohms, precision wire wound	1V11	5651
1R9, 1R10	470 ohms, 1 watt	1L1	5 henry 100 milliamps filter choke
1R11, 1R12	47,000 ohms, 1 watt	T1	Stancor power transformer type P6143
1R13	60,000 ohms, 1 watt	T2	Westinghouse power transformer (Navy type No. CAY-301164)
1R14	470,000 ohms, 1 watt	1P1	15,000 ohms wire wound potentiometer
1R15	15,000 ohms, precision wire wound	1P2	500,000 ohms carbon potentiometer
1R16	1 megohm, precision wire wound	1P3	10,000 ohms wire wound potentiometer
1R17	50,000 ohms, precision wire wound	1P4	800 ohms 25 watt rheostat
1R18	25,000 ohms, precision wire wound	1P5	800 ohms 15 turn Helipot
1R19	Sufficiently small to cause relay to close in case of excessive voltage rise during operation	1M1	0-200 milliamper meter
1R20	680,000 ohms, 1 watt	1S1	S.P.S.T. toggle switch
1R21 to 1R30	750 ohms, 10 watt	1S2	Single pole relay, normally open
1R31	0.65 ohm (wound with nichrome wire)	1S3	S.P.S.T. toggle switch
1C1	8 mfd 600 v	1S4	Single pole 11 position rotary switch
1C2	12 mfd 600 v	1S5	D.P.D.T. toggle switch
1C3	20 mfd 600 v		

² J. M. McCrea and D. J. LeRoy, Rev. Sci. Inst. 19, 692 (1948).

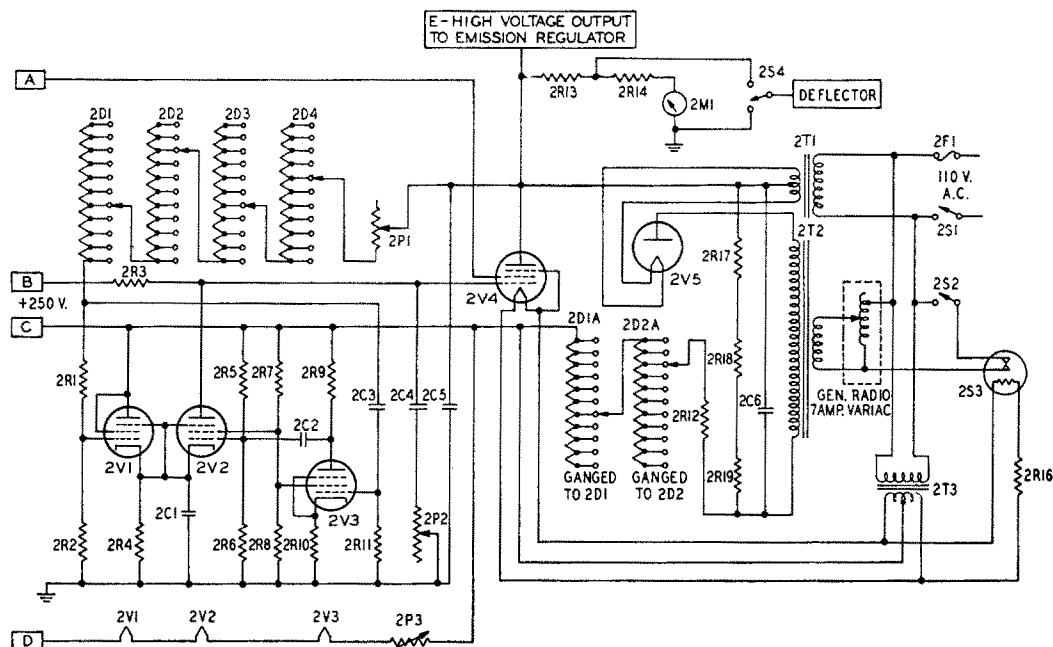


FIG. 2. Parts list for high voltage supply.

2R1	250,000 ohms, precision wire wound	2V1, 2V2, 2V3	12AU6
2R2, 2R6, 2R8	75,000 ohms, precision wire wound	2V4	Type 813 transmitting tube
2R3	1 megohm, precision wire wound	2V5	Type 8020 high voltage rectifier
2R4	25,000 ohms, precision wire wound	2C1	0.01 mfd 600 v
2R5	50,000 ohms, precision wire wound	2C2	0.25 mfd 400 v
2R7	35,000 ohms, precision wire wound	2C3	2 mfd 600 v
2R9	30,000 ohms, precision wire wound	2C4	0.1 mfd 600 v
2R10	40,000 ohms, precision wire wound	2C5	4 mfd 3000 v
2R11	2.2 megohms carbon 1 watt	2C6	4 mfd 4000 v
2R12	50,000 ohms, 100 watt	2T1	Stancor filament transformer type P-4086, 5 v c.t. 14 amp, 10,000 v insulation
2R13, 2R14	2 megohms, precision wire wound	2T2	Maloney Electric Company high voltage transformer part No. 5503 (Army surplus) 5600 v at 0.1 amp. (reduced to 3700 v with 1 kva Variac)
2R16	Reduces 10 v to 6 v required by 2S3 relay	2T3	Stancor filament transformer type 6139 10 v c.t. 8 amp.
2R17, 2R18, 2R19	10 megohms, 2 watt	2T4	General Radio variac 7½ amp. capacity
2D1A	10 steps, 5000 ohms per step (10 watt each)	2M1	0-1 milliamp. meter
2D2A	10 steps, 470 ohms per step (2 watt each)	2S1	S.P.S.T. toggle switch
2D1	10 steps, 100,000 ohms per step precision wire wound	2S2	S.P.S.T. toggle switch—high voltage on-off
2D2	10 steps, 10,000 ohms per step precision wire wound	2S3	Amperite thermostatic delay relay type 6N045
2D3	General Radio decade type 510E 1000 ohms per step	2S4	S.P.S.T. high voltage rotary switch for beam on-off
2D4	General Radio decade type 510D 100 ohms per step		
2P1	100 ohms, wire wound potentiometer		
2P2	3 megohms, carbon potentiometer		
2P3	1300 ohms, 50 watt potentiometer		

automatic magnetic scanning for the desired mass range.

HIGH VOLTAGE SUPPLY

The high voltage supply shown in Fig. 2 furnishes a continuously variable regulated voltage in the range 600 to 2200 volts for accelerating the ions in the mass spectrometer. The voltage of the output is varied by means of decades 2D1 to 2D4, which are ganged with 2D1A and 2D2A to keep the load across the rectifier and transformer nearly constant. Condenser 2C4 and resistor 2P2 are included to eliminate tendencies for oscillation. Tube 2V3 performs the function of applying part of the output ripple in a degenerative manner to the grid of 2V2 which in turn acts to reduce the ripple of the output. A 1 percent variation in the line voltage appears as a 0.001 percent variation of output at 600 volts and as 0.005 percent at 2200 volts, with internal resistances of 1 and 4 ohms respectively at these outputs.

The reference voltage of 250 volts, the heater current for control tubes 2V1, 2V2, and 2V3, and the other

necessary voltages are obtained from the appropriate places in the magnet power supply (C, D, A, and B). The thermal time delay relay 2S3 protects the cathodes of 2V4 and 2V5.

THE ELECTRON EMISSION REGULATOR

The emission regulator circuit as shown in Fig. 3 consists of two parts. One part is a power supply similar to the one used in the magnet circuit. Since the requirements for this power supply are less critical than the one used for furnishing current to the magnet windings, the plate supply voltage for the amplifier tube (3V12) is obtained from the unregulated direct current from the rectifiers. This power supply provides the electron accelerating voltage and the trap voltage in the ion source.

Regulation of electron emission of the filament in the source is accomplished by the second part of the emission regulator. Electron emission currents from the filament in the ion source flows through resistors 3R10 and 3P2 and the resulting voltage drop is amplified and applied to the grid of a series control tube (3V14) which

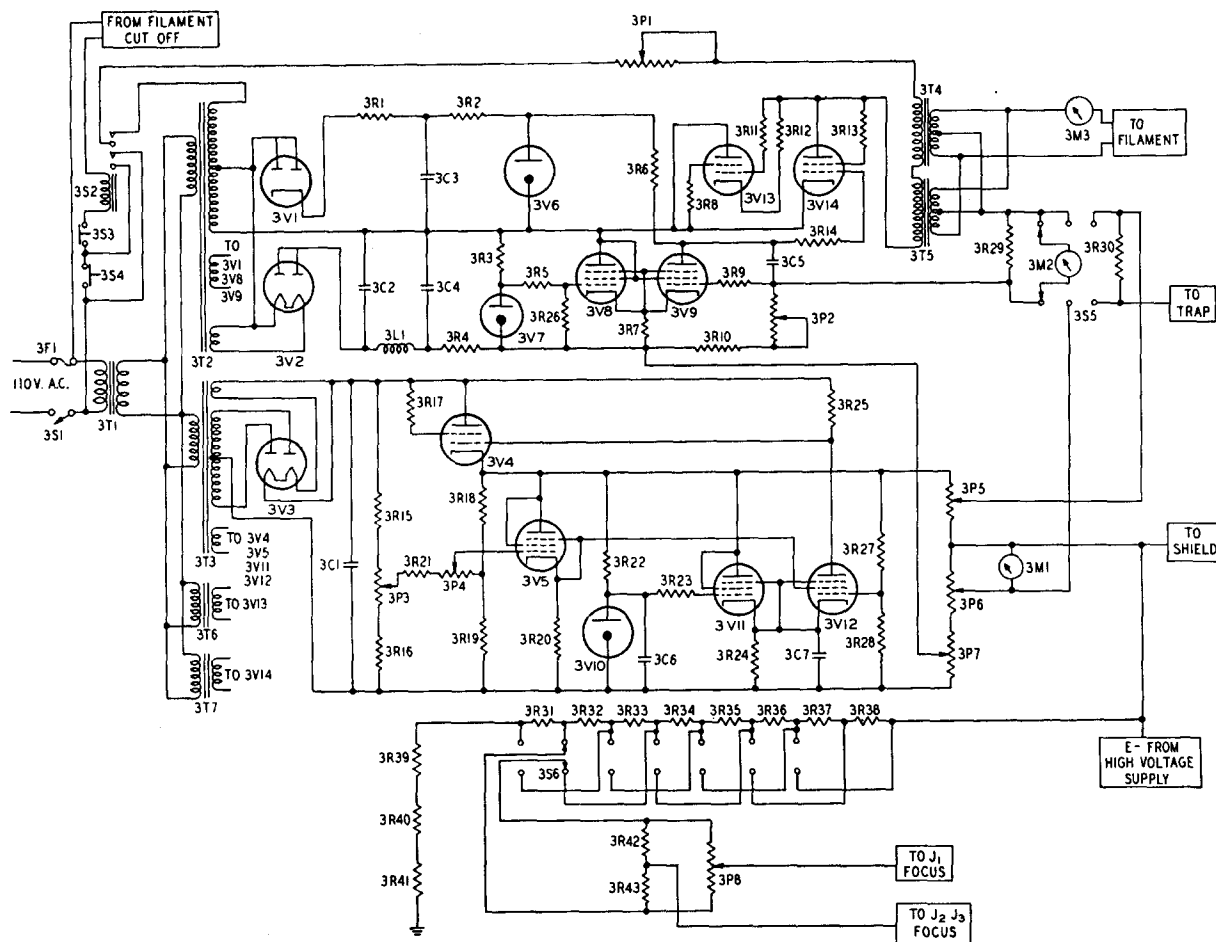


Fig. 3. Parts list for emission regulator.

3R1	300 ohms, 10 watt	3P4	0.5 megohm, carbon potentiometer
3R2	35,000 ohms, 20 watt	3P5	5000 ohms, wire wound
3R3	7500 ohms, 10 watt	3P6	10,000 ohms, wire wound
3R4	5000 ohms, 10 watt	3P7	5000 ohms, wire wound
3R5	25,000 ohms, precision wire wound	3P8	3 megohm, carbon potentiometer
3R6	0.5 megohm, precision wire wound	3T1	Thordarson No. T18V01 1:1 isolation transformer (changes made so secondary is insulated for 3500 v) 250 volt-ampere capacity
3R7	15,000 ohms, precision wire wound	3T2	Acme No. T4822 power transformer
3R8, 3R13	15,000 ohms, 2 watt	3T3	Stancor No. P6143 power transformer
3R9, 3R11, 3R14	82,000 ohms, 1 watt	3T4, 3T5	6.3 volt, 5 amperes filament transformers
3R10	150,000 ohms, 1 watt	3T6, 3T7	6.3 volt, 2 amperes filament transformers
3R12	50 ohms, 5 watt	3C1, 3C3	16 mfd 600 v
3R15, 3R19, 3R20, 3R22	68,000 ohms, 1 watt	3C2, 3C4	8 mfd 600 v
3R16	27,000 ohms, 1 watt	3C5	0.05 mfd 600 v
3R17	470 ohms, 2 watt	3C6, 3C7	0.01 mfd 400 v
3R18	47,000 ohms, 1 watt	3M1	0-100 volts d.c. voltmeter
3R25	2.2 megohms, 1 watt	3M2	0-100 microampere d.c.—1000 ohms resistance
3R26	75,000 ohms, precision wire wound	3M3	0-10 a.c. amperes
3R27	50,000 ohms, precision wire wound	3V1	6X4
3R24, 3R28	35,000 ohms, precision wire wound	3V2, 3V3	5Y3
3R29	250 ohms, precision wire wound.	3V4	6L6
	Shunts meter 3M2 to read 500 microamperes full scale	3V5, 3V8, 3V9, 3V12	6AU6
3R30	1000 ohms, precision wire wound.	3V6, 3V7	0A2 miniature voltage regulator tube
	Shunts meter 3M2 to read 200 microamperes full scale	3V10	5651 miniature voltage regulator tube
3R21, 3R23, 3R31 to 3R38	0.47 megohm, 1 watt	3V11	6AG5
3R39, 3R40, 3R41	10 megohms, 1 watt	3V13, 3V14	807
3R42, 3R43	2.2 megohms, 1 watt	3S1	S.P.S.T. toggle on-off switch
3P1	800 ohms, 25 watt rheostat	3S2	D.P.D.T. high voltage relay
3P2	250,000 ohms, carbon potentiometer	3S3	Push switch normally closed
3P3	15,000 ohms, wire wound potentiometer	3S4	Push switch normally open
		3S5	2 pole three position switch
		3S6	2 pole seven position switch

controls the current flowing through the primary of transformers 3T4 and 3T5. The secondaries of these transformers supply the current to the filament in the mass spectrometer. Tube 3V13 serves to maintain proper wave form of the primary current. The controlled

range of electron emission from the filament in the mass spectrometer extends from 100 to 500 microamperes depending upon the setting of 3P2. A 1 percent change in line voltage input results in a 0.02 percent change in average emission. Switch 3S5 is a three-position switch

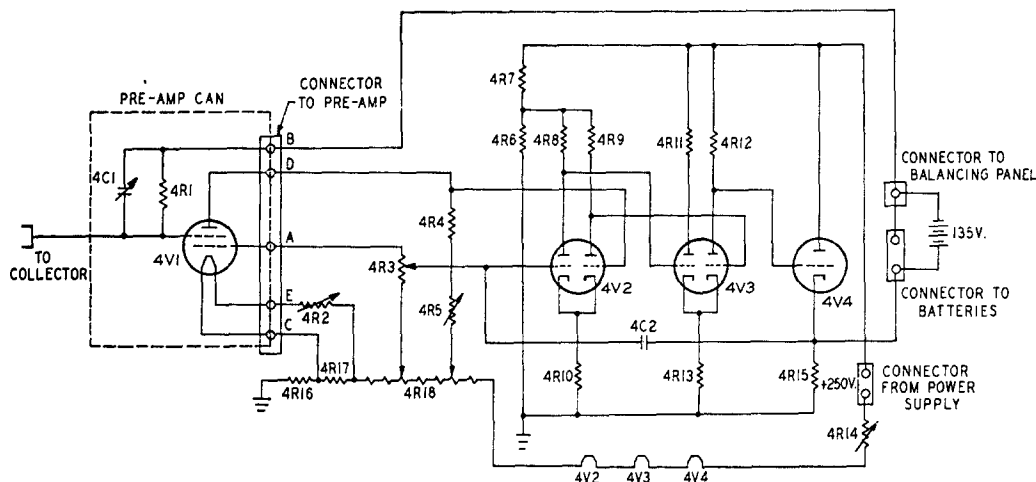


Fig. 4. Parts list for d.c. amplifier.

4R1	1.5×10 ¹⁰ ohm Victoreen Hi-Megohm obtained from Victoreen Instrument Company, Cleveland, Ohio	4R14	1000 ohms, 50 watt
4R2	30 ohm wire wound potentiometer	4R15	25,000 ohms, precision wire wound
4R3	20,000 ohms Helipot 10 turns, obtained from Helipot Corporation, South Pasadena, California	4R16	80 ohms, special wire wound
4R4	250,000 ohms, precision wire wound	4R17	40 ohms, special wire wound
4R5	100,000 ohms Helipot 15 turns	4R18	12 steps of 26 ohms each special wire wound
4R6	20,000 ohms, precision wire wound	4V1	VX-41A obtained from Victoreen Instrument Company, Cleveland, Ohio
4R7	35,000 ohms, precision wire wound	4V2	12SL7-GT
4R8, 4R9	500,000 ohms, precision wire wound	4V3	12SL7-GT
4R10	75,000 ohms, precision wire wound	4V4	12J5-GT
4R11, 4R12	1 megohm, precision wire wound	4C1	100 micro-microfarad variable air dielectric condenser
4R13	300,000 ohms, precision wire wound	4C2	0.002 mfd condenser 400 v

which allows meter 3M2 to read either trap current, total emission current or to indicate the zero adjustment of 3P6 so that meter 3M1 reads electron accelerating voltage.

ION CURRENT AMPLIFICATION

Essentially the same amplifier design as described by Nier was used initially in this research. A stable d.c. amplifier is obtained by using our previously described power supply and by using the tubes described in Fig. 4. To allow collection of currents of approximately 3.7×10^{-9} and 1.5×10^{-11} ampere for masses 44 and 46 respectively, and to get sensitivity of 0.2 permil in determining the ratio of mass 46 to mass 44, the respective sizes of the resistors 4R1 of the two amplifiers must be approximately 1.5×10^{10} and 1.5×10^{11} ohms.

Since the inherent difficulties present in sensitive d.c. amplifiers did not permit day to day use of the mass spectrometers for analyses with the accuracy required in this research, a different amplification system was tried. A vibrating reed electrometer with its associated amplifier in conjunction with a null system described by Nier, Ney, and Inghram,³ where the vibrating reed replaces the FP54 electrometer, gave continuously satisfactory performance.

A schematic diagram of this system is given in Fig. 5.

GAS FEED AND RECORDING POTENTIOMETER

Since the amplifiers always drift with time and have a noise level as high as or higher than the sensitivity re-

quired, it is necessary to have a record of the state of balance of the potentials produced by the two peaks being compared, and it is necessary to be able to change from one sample to another very rapidly.

Two complete feed systems with gas volumes, mercury leveling reservoirs, and capillary leaks of the type previously described by Nier were attached to the mass spectrometer through a magnetically operated valve which delivered one sample to the mass spectrometer and the other to a waste vacuum line. In this way the flow of the two samples could be reversed rapidly. Since the valve is on the high vacuum side of the leaks there is a very small lag in changing from one sample to the other. The tube leading from the valve to the mass spectrometer must be fairly large in order that the hold up in this region is small. In our instrument the volume of the valve and connecting tube is about 10 cc and the internal diameter and length of the feed tube within the mass spectrometer head are 3 mm and 12 cm, respectively. The greater resistance of a 2-mm I.D. tube considerably increased the time lag. The gases replace each other in a few seconds. The construction of the valve is shown in Fig. 6. The memory effect of each gas is small and hence when samples of nearly identical composition (differing by, say, 5 permil in the ratio) are compared, this effect is insignificant. However, if samples of substantially different isotopic composition are used, say differing by a few percent in the ratio, then some minutes must elapse before steady conditions are established. If carbon dioxide containing oxygen of double the normal concentration or higher is used, the

³ Nier, Ney, and Inghram, Rev. Sci. Inst. 18, 294 (1947).

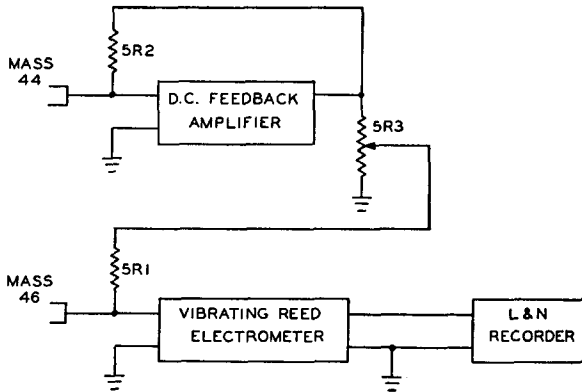


FIG. 5. Parts list for ion beam balancing circuit. 5R1— 1.5×10^{11} ohms, Victoreen Hi-Megohm resistor. 5R2— 1.5×10^{10} ohms, Victoreen Hi-Megohm resistor. 5R3—Put and take decade resistance potentiometer, made up of General Radio decade resistance units 510A, 510B, 510C, 510D and 510E. Vibrating reed electrometer—obtained from The Applied Physics Corporation, 30 West Green Street, Pasadena, California. D. c. feedback amplifier—as shown in Fig. 4.

feed system that contained the concentrated gas will contaminate succeeding samples so that analysis to high precision, i.e., differences of the order of 0.2 permil in the ratio, cannot be made until the apparatus has been pumped and swept out for many days.

It is not possible to judge the steadiness of the balance of the two potentials by watching a galvanometer when it is desired to detect differences of the order of the unsteadiness of the potentials being observed. The galvanometer fluctuates unsteadily, and whether the mean has any reliable meaning cannot be judged. The recording potentiometer makes a trace which can be averaged over a satisfactory period of time.

We have used recording potentiometers to observe the balance between the potentials of the two peaks. The recorder draws an irregular line down the chart with negligible drift (if the instrument is in proper adjustment). If erratic fluctuations occur the instrument is unreliable. Of course, if the small but statistically regular fluctuations are too great the precision desired cannot be secured. By observing the record for some time it is possible to judge the stability of the amplifier circuits particularly as well as the mass spectrometer as a whole, and thus decide whether analyses can be made.

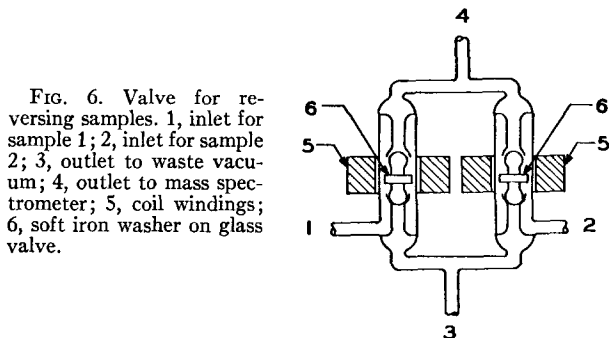


FIG. 6. Valve for reversing samples. 1, inlet for sample 1; 2, inlet for sample 2; 3, outlet to waste vacuum; 4, outlet to mass spectrometer; 5, coil windings; 6, soft iron washer on glass valve.

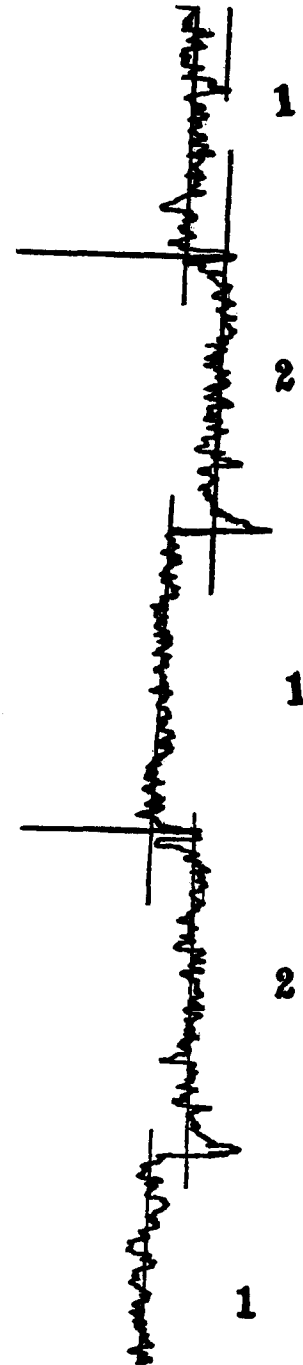


FIG. 7. Sample potentiometer record.

The use of the recording potentiometers is essential to securing differences to a precision of 0.2 permil of the oxygen isotope ratio.

The type of traces obtained are shown in Fig. 7, where trace 2 represents the null point of the standard and trace 1 represents the deviation from the null point by an increase of 0.63 permil in the intensity of ion beam of mass 46. If the deviation from the null point was large, part of the increase or decrease in mass 46 was taken up by changing the setting on the decade resistor system. Straight lines are drawn through the irregular

TABLE I.

Sample	CO ₂ gas		CO ₂ gas		Sample	O ₂ gas	
	δ(O ¹⁸)	Date	δ(C ¹³)	Date		δ(O ¹⁸)	Date
1	-0.53	12/13/49	0.42	12/13/49	1	17.11	12/7/49
	-0.59	1/4/50	0.50	1/4/50		16.77	12/8/49
2	-2.98	12/20/49	1.95	12/20/49	2	0.23	2/10/50
	-2.99	1/3/50	1.75	1/3/50		-0.10	2/13/50
	-3.00	1/3/50	1.58	1/3/50			
3	-3.87	12/12/49	1.30	12/12/49	3	0.00	2/10/50
	-3.83	1/3/50	1.35	1/3/50		0.00	2/11/50
4					4	-0.20	2/13/50
	-2.30	12/13/49	2.30	12/13/49		0.44	2/10/50
	-2.56	1/4/50	2.46	1/4/50		-0.02	2/11/50
5						-0.14	2/13/50
	-2.18	12/22/49	1.73	12/22/49			
	-2.22	1/4/50	1.90	1/4/50			

curves and extended to the point where the samples were changed and the differences are read at these points. The displacement on the chart is easily calibrated in terms of the dial settings in the resistance panel. The average of some five or seven readings is then used to correct the ratio read from the resistances.

CONCLUSION

Two instruments of this type have been constructed and operated, one for 18 months, the other for 6 months. At present electronics technicians can keep the instruments in operation from 50 to 75 percent of the time. The analyses are made by laboratory technicians. Altogether some two thousand high precision comparisons of oxygen isotopic abundances in carbon dioxide, some hundreds of carbon abundances in the same gas, and perhaps a hundred comparisons of oxygen isotopes in oxygen gas have been made with these instruments. Examples of check analyses are given in Table I. The

recorded figures are the differences in permils of the normal ratios between the sample and the standard working gas, i.e.,

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000,$$

where R_{sample} and R_{standard} are the ratios of CO¹⁶O¹⁸ to CO₂¹⁶ for the unknown sample and reference gas respectively. These examples of analysis on carbon dioxide are taken from our working notebooks and are a group of consecutive duplicate analyses selected at random and with no omission of any results. These duplicate analyses are on different preparations of the gas from the same samples of calcium carbonate and hence the fluctuations include any variations due to the chemical preparation of the gas. (The calcium carbonate is heated to 475°C for 15 minutes in a stream of pure helium gas and the carbon dioxide liberated by reaction of the carbonate with 100 percent orthophosphoric acid.) Thus the operation of the instrument is at least as reproducible as indicated by these results. On the basis of analyses made before the vibrating reed amplifier was adapted to the instrument, we believe that variations greater than 0.2 permil are due to variations introduced by the method of preparing the gas, a subject which will be discussed elsewhere.

The first example of the oxygen gas analyses is for two preparations from a silicate rock. The last three examples are all for tank oxygen. The most recent of our analyses are given here since they represent the precision we have been able to attain in our most recent work. It is expected that this precision will be maintained and in fact improved in the future as we acquire more experience in these analyses.