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 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.

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

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. 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

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**FIG. 1. Power supply (regulated).**

- **1R1** 13,500 ohms, 10 watt, wire wound
- **1R2** 5000 ohms, 10 watt, wire wound
- **1R3** 65,000 ohms, 1 watt
- **1R4** 39,000 ohms, 1 watt
- **1R5** 22 megohms, 1 watt
- **1R6** 50,000 ohms, precision wire wound
- **1R7** 75,000 ohms, precision wire wound
- **1R8** 35,000 ohms, precision wire wound
- **1R9, 1R10** 470 ohms, 1 watt
- **1R11, 1R12** 47,000 ohms, 1 watt
- **1R13** 60,000 ohms, 1 watt
- **1R14** 470,000 ohms, 1 watt
- **1R15** 15,000 ohms, precision wire wound
- **1R16** 1 megohm, precision wire wound
- **1R17** 50,000 ohms, precision wire wound
- **1R18** 25,000 ohms, precision wire wound
- **1R19** Sufficiently small to cause relay to close in case of excessive voltage rise during operation
- **1R20** 680,000 ohms, 1 watt
- **1R21** to 1R30 750 ohms, 10 watt
- **1R31** 0.65 ohm (wound with nichrome wire)
- **1C1** 8 mfd 600 v
- **1C2** 12 mfd 600 v
- **1C3** 20 mfd 600 v
- **1C4** 0.001 mfd 600 v
- **1C5** 0.01 mfd 400 v
- **1C6** 250 micro-microfarad
- **1C7** 0.0001 mfd 400 v
- **1V1** 6L6
- **1V2, 1V3** 5U4G
- **1V4, 1V5** 6L6
- **1V6, 1V7, 1V8, 1V9** OA2
- **1V10, 1V12, 1V13** 12AU6
- **1V11** 5651
- **1L1** 5 henry 100 milliamperes filter choke
- **1T1** Stancor power transformer type P6143
- **1T2** Westinghouse power transformer (Navy type No. CAY-301164)
- **1P1** 15,000 ohms wire wound potentiometer
- **1P2** 500,000 ohms carbon potentiometer
- **1P3** 10,000 ohms wire wound potentiometer
- **1P4** 800 ohms 25 watt rheostat
- **1P5** 800 ohms 15 turn Helipot
- **1M1** 0-200 milliamperes meter
- **1S1** S.P.S.T. toggle switch
- **1S2** Single pole relay, normally open
- **1S3** S.P.S.T. toggle switch
- **1S4** Single pole 11 position rotary switch
- **1S5** D.P.D.T. toggle switch

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*J. M. McCrea and D. J. LeRoy, Rev. Sci. Inst. 19, 692 (1948).*
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 660 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 660 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
Improvements in Mass Spectrometers

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. 3. Parts list for emission regulator.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>3R1</td>
<td>300 ohms, 10 watt</td>
<td></td>
</tr>
<tr>
<td>3R2</td>
<td>35,000 ohms, 20 watt</td>
<td></td>
</tr>
<tr>
<td>3R3</td>
<td>75,000 ohms, 10 watt</td>
<td></td>
</tr>
<tr>
<td>3R4</td>
<td>50,000 ohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R5</td>
<td>25,000 ohms, precision wire wound</td>
<td></td>
</tr>
<tr>
<td>3R6</td>
<td>0.5 megohm, precision wire wound</td>
<td></td>
</tr>
<tr>
<td>3R7</td>
<td>15,000 ohms, precision wire wound</td>
<td></td>
</tr>
<tr>
<td>3R8, 3R13</td>
<td>15,000 ohms, 2 watt</td>
<td></td>
</tr>
<tr>
<td>3R9, 3R11, 3R14</td>
<td>82,000 ohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R10</td>
<td>150,000 ohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R12</td>
<td>50,000 ohms, 5 watt</td>
<td></td>
</tr>
<tr>
<td>3R15, 3R19, 3R20, 3R22</td>
<td>68,000 ohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R16</td>
<td>27,000 ohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R17</td>
<td>470 ohms, 2 watt</td>
<td></td>
</tr>
<tr>
<td>3R18</td>
<td>47,000 ohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R19</td>
<td>2,2 megohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R20</td>
<td>75,000 ohms, precision wire wound</td>
<td></td>
</tr>
<tr>
<td>3R21</td>
<td>50,000 ohms, precision wire wound</td>
<td></td>
</tr>
<tr>
<td>3R22</td>
<td>35,000 ohms, precision wire wound</td>
<td></td>
</tr>
<tr>
<td>3R23</td>
<td>250 ohms, precision wire wound, Shunt meter 3M2 to read 500 microamperes full scale</td>
<td></td>
</tr>
<tr>
<td>3R30</td>
<td>1000 ohms, precision wire wound, Shunt meter 3M2 to read 500 microamperes full scale</td>
<td></td>
</tr>
<tr>
<td>3R24, 3R28</td>
<td>0,47 megohm, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R25</td>
<td>10 ohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R26</td>
<td>2.2 megohms, 1 watt</td>
<td></td>
</tr>
<tr>
<td>3R27</td>
<td>800 ohms, 25 watt</td>
<td></td>
</tr>
<tr>
<td>3P1</td>
<td>250,000 ohms, carbon potentiometer</td>
<td></td>
</tr>
<tr>
<td>3P2</td>
<td>15,000 ohms, wire wound potentiometer</td>
<td></td>
</tr>
</tbody>
</table>
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 $3.7 \times 10^{-9}$ and $1.5 \times 10^{-11}$ amperes 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 $1.5 \times 10^9$ and $1.5 \times 10^{11}$ 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, 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 required, 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

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Footnote:

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
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 permls of the normal ratios between the sample and the standard working gas, i.e.,

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

where \( R_{\text{sample}} \) and \( R_{\text{standard}} \) are the ratios of CO\textsuperscript{14}O\textsuperscript{18} to CO\textsuperscript{12}O\textsuperscript{18} 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.

**Table I.**

<table>
<thead>
<tr>
<th>CO\textsubscript{2} gas Sample</th>
<th>4(O\textsuperscript{18})</th>
<th>Date</th>
<th>CO\textsubscript{2} gas Sample</th>
<th>4(C\textsuperscript{13})</th>
<th>Date</th>
<th>O\textsubscript{2} gas Sample</th>
<th>4(O\textsuperscript{18})</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.53</td>
<td>12/13/49</td>
<td>0.42</td>
<td>12/13/49</td>
<td>1</td>
<td>17.11</td>
<td>12/7/49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.59</td>
<td>1/4/50</td>
<td>0.50</td>
<td>1/4/50</td>
<td>2</td>
<td>0.23</td>
<td>2/10/50</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-2.98</td>
<td>12/20/49</td>
<td>1.95</td>
<td>12/20/49</td>
<td>3</td>
<td>0.00</td>
<td>2/10/50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2.99</td>
<td>1/3/50</td>
<td>1.75</td>
<td>1/3/50</td>
<td>4</td>
<td>0.23</td>
<td>2/10/50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.00</td>
<td>13/50</td>
<td>1.58</td>
<td>13/50</td>
<td>5</td>
<td>-0.14</td>
<td>2/13/50</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-3.87</td>
<td>12/12/49</td>
<td>1.30</td>
<td>12/12/49</td>
<td>6</td>
<td>0.00</td>
<td>2/10/50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.83</td>
<td>1/3/50</td>
<td>1.35</td>
<td>1/3/50</td>
<td>7</td>
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<td>2/13/50</td>
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</tr>
<tr>
<td>4</td>
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<td>12/13/49</td>
<td>2.30</td>
<td>12/13/49</td>
<td>8</td>
<td>0.44</td>
<td>2/10/50</td>
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<tr>
<td></td>
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<td>2.46</td>
<td>1/4/50</td>
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<td>-2.12</td>
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<td>1.90</td>
<td>13/50</td>
<td>10</td>
<td>-0.14</td>
<td>2/13/50</td>
<td></td>
</tr>
</tbody>
</table>

This table shows that the analyses are reproducible and consistent within the limits of error.