

A GAS CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF TRACE AMOUNTS OF CARBON

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The high sensitivity of the gas chromatographic technique makes it an ideal tool for application in the field of micro or trace analysis. Even using a conventional thermoconductivity detector, which by standards of gas chromatography is considered to be of low sensitivity, measurements of matter in micro- and submicro-gram region can be executed. The incorporation of gas chromatographic techniques into microanalytical procedures can greatly enlarge the field of microanalysis and provide logical extension to the field of ultramicroanalysis.

Unfortunately, microanalysts of today do not utilize this powerful tool to its greatest advantage. Only a few publications¹⁻⁵ dealing with the use of gas chromatography in the field of classical microanalysis have appeared in recent years.

In the field of metallurgy, where trace analysis, especially of hydrogen, oxygen, carbon and nitrogen, plays an important role, the potentials of gas chromatography are finally being recognized. A number of papers dealing with this analytical technique for the analysis of trace impurities in metals were presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in the spring of 1962.

MOONEY AND GARBINI⁶ were able to determine carbon in metals by means of combustion of a sample in an induction furnace, collection of the products of combustion plus oxygen in a liquid nitrogen trap, followed by the gas chromatographic determination of intrapped material using a conventional Perkin-Elmer instrument. FASSEL AND MONTE⁷ determined oxygen and nitrogen content of metals using a high-current D.C. carbon-arc discharge in a static atmosphere of helium. A portion of the resulting gas mixture was analyzed using a commercially available gas chromatograph.

SCHULTZ⁸ determined nitrogen in metals by fusing the sample in a graphite crucible and transferring the resulting gases into a chromatograph cell with an inert gas for separation and determination.

The purpose of this study was to design and build a unitized analytical instrument for the determination of impurities in metals. The instrumental system consists of a specially designed gas chromatograph integrated with a commercial model induction furnace to form a relatively compact unit, capable of rapid accurate analyses.

The operating model of such an instrument was tested for analysis of carbon in metals. The studies on future use of this instrument for determination of oxygen, nitrogen and hydrogen in metals are in progress at the present time in this laboratory.

EXPERIMENTAL

Chemicals

1. Copper ring accelerator—Leco 550-184.
2. Tin metal accelerator—Leco 501-76.
3. Iron chip accelerator—Leco 501-77.
4. Carbon dioxide gas.
5. Liquid argon.
6. Helium and oxygen.

*Apparatus and equipment**1. Induction furnace, Leco Model No. 537*

A Leco induction furnace is used for combustion of the sample. The gas stream outlet of the furnace is connected to the Beckman sampling valve and trap. The commercial grade of oxygen gas was found to contain a sufficient amount of impurities to produce a significant blank. A conventional purification train using a copper oxide tube heated to 500°, followed by an ascarite tube, reduced the blank considerably but failed to eliminate it completely. For this reason, a tube containing decomposed silver permanganate prepared by a procedure of LYSYJ AND ZAREMBO⁹ heated at 500° will be used instead of copper oxide for future work. The flow system of the combustion train is shown in Fig. 1.

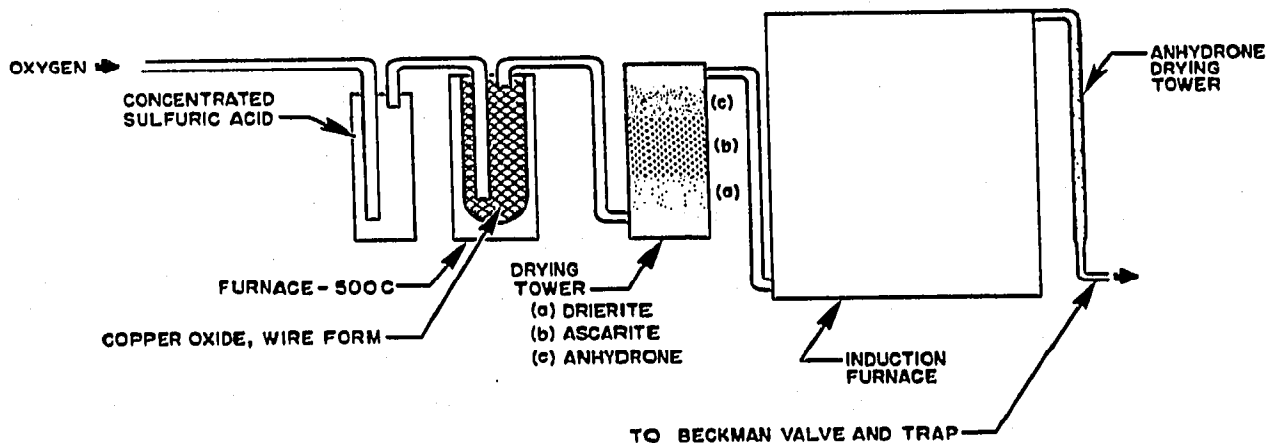


Fig. 1. Induction furnace and purification train.

2. Special gas chromatograph

The instrument is housed in a 20 × 15 × 15 in. aluminum box and incorporates a thermistor Gow-Mac thermoconductivity cell and a Beckman sample valve for collection and introduction of the sample into the helium stream. The thermoconductivity cell Gow-Mac 9677 (AEL) and gas chromatographic column are housed in a Dewar flask, equipped with heating tape and a precision temperature regulator. For the analysis of carbon in metals, a 26 in. long, 3/16 in. diameter copper tube filled with silica gel, 20–200 mesh size, is used. The design of the separating and detecting portion of the instrument is shown in Fig. 2.

To permit collection and introduction of the sample into the helium stream, a Beckman two-way sampling valve was modified in such a way as to permit the

application of a cold trap over the collecting loop. Two stainless steel U-tubes, 1/4 in. diameter and 3 in. long, were incorporated in the valve. By manipulating the position of the valve, one tube is placed in the helium stream and the second in the oxygen stream coming from the exit side of the induction furnace where combustion of the

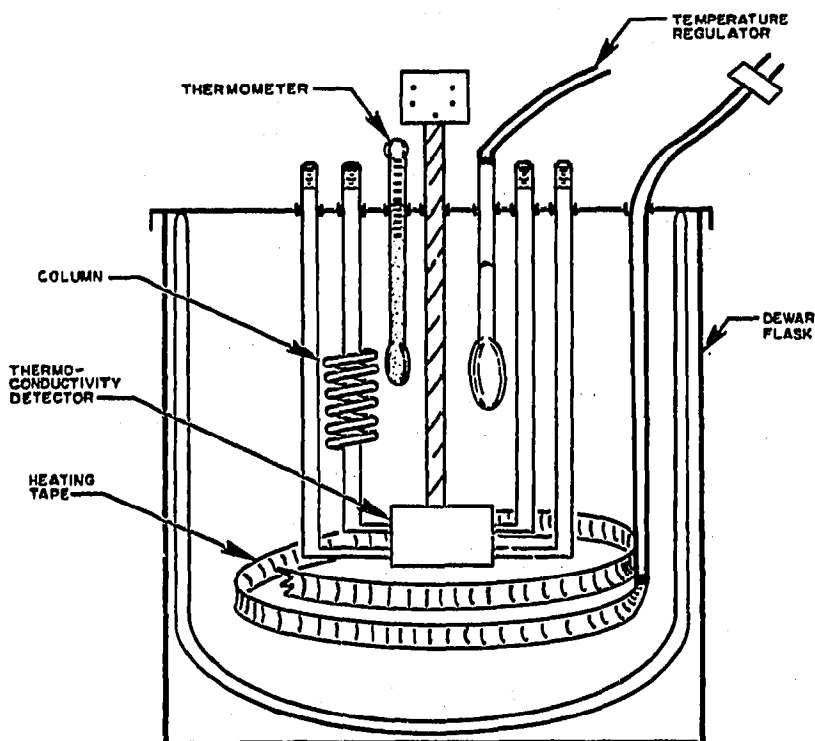


Fig. 2. Detector housing.

sample is conducted. When the liquid argon trap is placed over the collecting tube, carbon dioxide and small amounts of oxygen are condensed. After removal of oxygen by pumping, the carbon dioxide is vaporized and introduced in the helium stream by changing the position of the valve.

A single stream of helium is used in the design of the gas chromatograph. The carrier gas passes first through the reference side of the detecting cell, then through the collecting valve, column, and finally through the detector side of the thermoconductivity cell. The flow system was constructed from 3/16 in. copper tubing and is shown in Fig. 3. The electrical circuit is shown in Fig. 4.

3. Leeds & Northrup recorder, Speedomax Model G
4. Printing integrator, Perkin-Elmer Model 194
5. Thermocouple vacuum gauge and control (NRC Equipment Corp.)
6. Ceramic crucibles, Leco S28-35
7. Vacuum pump, Kinny
8. Rotometer flowmeters, Fisher & Porter No. 9143 and 9144
9. Oxygen purifying train.

PROCEDURE

The steel sample, containing 1 mg or less of carbon, is accurately weighed and placed into the ceramic crucible. Then 1.150 g (± 10 mg) each of the tin metal and iron chip

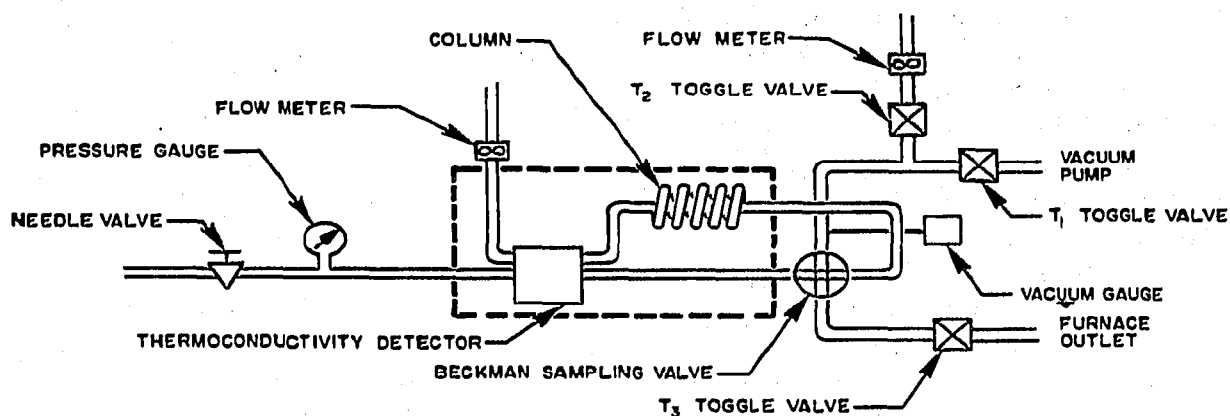


Fig. 3. Flow system of gas chromatograph.

accelerators are added to the sample, followed by one copper ring. It is essential to weigh the catalysts accurately, since they contain sufficient carbon to register an appreciable blank count. The sample is introduced into the furnace, and the apparatus is purged with pre-purified oxygen for 5 min at a rate of flow of 950 ml/min. The carbon dioxide trap is then immersed in liquid argon. The furnace is turned on and left at the maximum setting approximately 1700°C for 3 min and turned off. The entire apparatus is finally purged for an additional 2 min at the same rate of oxygen flow. The carbon dioxide trap is then isolated from the induction furnace by closing

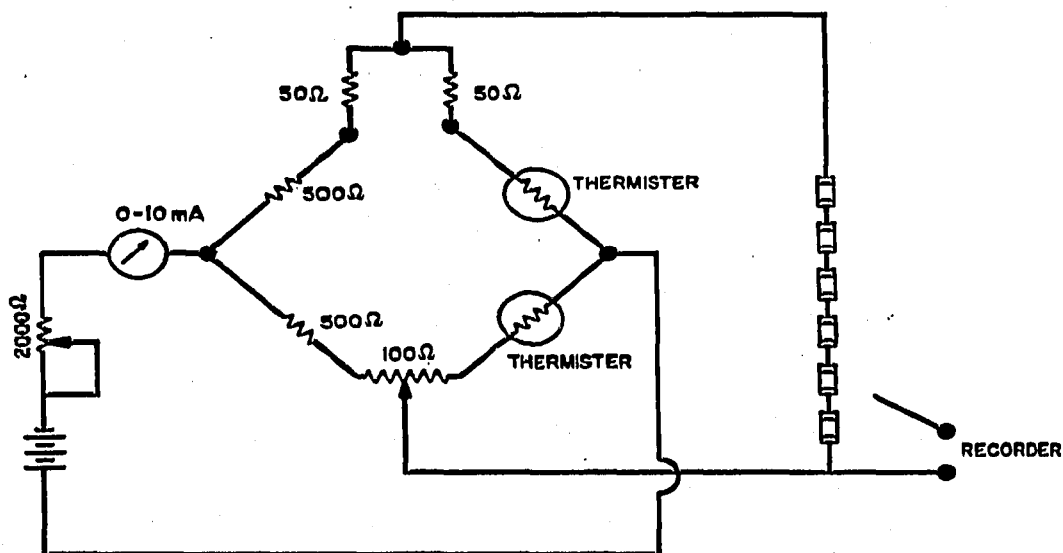


Fig. 4. Detection system electrical circuit.

a toggle valve and evacuated to a pressure of 1-2 mm of mercury to remove most of the oxygen. A small amount of oxygen actually condenses in the trap during the run, although its boiling point is only 2° higher than that of argon; therefore, it was found essential to include this evacuation step to avoid flooding the column. The vapor pressure of carbon dioxide at liquid argon temperature is $4 \cdot 10^{-6}$ mm of Hg, so there exists little danger, except for mechanical loss, of losing any carbon dioxide by vaporization. The Beckman valve is then rotated to place the carbon dioxide trap in

the helium stream, and the liquid argon trap is replaced by a room temperature water bath to rapidly vaporize the carbon dioxide. The following operating parameters were used for every analysis:

Helium inlet pressure—8 lb./in².

Helium flow (exit)—54 ml/min

Column and detector block temperature—150°F

Current—6 mA.

The carbon dioxide peak appeared 1.5 min after warming the trap, and was preceded by a small peak due to residual oxygen left after the pumping operation.

The apparatus was initially tested for leaks by following the procedure outlined above, except that the furnace was not heated. The absence of any carbon dioxide peak indicated no carbon dioxide leakage from the atmosphere. However, it was noted that if the furnace was heated using a platinum crucible as a receptor for 3 min during the oxygen flow, a carbon dioxide peak appeared. This was attributed to small amounts of hydrocarbons in the oxygen which were not removed by the purifying train, but which apparently underwent oxidation at the high temperature existing in the induction furnace (approximately 1700° C) in contact with platinum.

RESULTS AND DISCUSSION

The experimental data presented in Table I were obtained using a sample of Bureau of Standards Steel No. 161, which contains 64 % nickel, 17 % chromium, 15 % iron, and 0.342 % carbon.

The precision of the data is considered quite good in view of the fact that inhomogeneities can exist in the carbon content of the small steel samples and the catalysts.

TABLE I
DETERMINATION OF CARBON IN NBS STEEL NO. 161

| Blank study | | | | | | | |
|----------------------------------------------------------------|----------------------------|-----------------------------------|-----|------------------------------------|-----|---------|-----|
| Oxygen blank (heated furnace) Catalyst + oxygen blank | Counts | | | | | | |
| | 61 | | 54 | | | Average | 356 |
| | 360 | 352 | 348 | 358 | 354 | | |
| Sample study | | | | | | | |
| Sample wt. (g) | μg of carbon | Total counts (corr. for blank) | | Counts/ μg of carbon | | | |
| 0.2232 | 763 | 1604 | | 2.10 | | | |
| 0.2096 | 717 | 1413 | | 1.97 | | | |
| 0.2086 | 713 | 1566 | | 2.20 | | | |
| 0.2210 | 756 | 1654 | | 2.18 | | | |
| 0.1119 | 383 | 796 | | 2.08 | | | |
| 0.1095 | 374 | 684 | | 1.83 | | | |
| 0.1174 | 402 | 830 | | 2.06 | | | |
| 0.0612 | 209 | 453 | | 2.17 | | | |
| 0.0610 | 209 | 443 | | 2.12 | | | |
| 0.0647 | 221 | 473 | | 2.14 | | | |
| Average 2.09 | | | | | | | |
| Average deviation: $S = 0.079$ | | | | | | | |

The sensitivity of the method can be increased to over 60 times that shown by adjusting the electronic attenuators in the system and by using the detector at a lower temperature. However, in view of the large blank values obtained, greater sensitivities would be less valuable.

The standardization of the instrument was done, also using carbon dioxide as a standard. Measured amounts of carbon dioxide were introduced in a helium stream and determined in the usual manner. The number of counts per microgram of carbon were calculated and presented in Table II. The instrument can also be used for ultramicro determination of carbon in organic matter.

TABLE II
DETERMINATION OF CARBON IN CARBON DIOXIDE GAS*

| | <i>mm pressure CO₂</i> | <i>μg of carbon</i> | <i>Number of counts</i> | <i>Counts/μg of carbon</i> |
|-----|---------------------------------------|-------------------------|-----------------------------|--------------------------------|
| 1. | 126 | 177.8 | 444 | 2.49 |
| 2. | 182 | 256.9 | 652 | 2.43 |
| 3. | 198 | 279.5 | 730 | 2.61 |
| 4. | 214 | 302.0 | 765 | 2.53 |
| 5. | 246 | 347.2 | 895 | 2.57 |
| 6. | 284 | 400.8 | 1001 | 2.49 |
| 7. | 387 | 546.2 | 1397 | 2.55 |
| 8. | 404 | 570.2 | 1424 | 2.49 |
| 9. | 424 | 598.4 | 1590 | 2.57 |
| 10. | 433 | 611.2 | 1598 | 2.61 |
| 11. | 438 | 618.2 | 1580 | 2.55 |
| 12. | 466 | 657.7 | 1662 | 2.52 |
| 13. | 539 | 760.7 | 1994 | 2.62 |
| 14. | 551 | 777.7 | 1978 | 2.54 |

Average 2.54

Average deviation = 0.045

* Volume of injection loop 19.9 ml. Analysis was done under slightly different operating conditions than standardization using NBS sample 161.

A study is being conducted on the use of the instrument essentially unchanged for the determination of oxygen in metals. The samples are ignited in a graphite crucible in an argon atmosphere in the usual manner, and the carbon dioxide collected and determined as before. The trap-evacuation step would be eliminated, since argon should not condense during the purging and sweeping operations.

An investigation is currently in progress on the determination of nitrogen in metals using a slightly modified apparatus. The carbon dioxide trap under the Beckman valve would be replaced by a trap containing Linde sieves or charcoal cooled with liquid nitrogen. The nitrogen evolved from the metal nitrides heated to high temperatures in a graphite crucible would be swept out with helium or hydrogen into the cooled packed column, and later eluted by warming the trap to room temperature.

SUMMARY

The design of a unitized analytical instrument for the determination of impurities in metals is described. The instrumental system consists of a specially designed gas

chromatograph integrated with the induction furnace to form a relatively compact unit, capable of rapid and accurate analyses.

The operating model of such an instrument was built and tested for analysis of trace amounts of carbon in metals.

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