# Comparison of Metal Bath Techniques in Vacuum Fusion Analysis by an Isotope Dilution Method

Hitoshi KAMADA and Keiichi FURUYA

*Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo*

(Received September 19, 1967)

Many applications of metal bath techniques to vacuum fusion analysis have been reported. In these reports, metal bath techniques are used to promote a reaction between carbon and oxygen in a flux and/or to eliminate a gettering action by the adsorptive elements evaporated from the samples. Beach and Guldner¹⁾ measured the effect of evaporated films of carbon, nickel, iron, germanium, platinum, aluminum, manganese and titanium on the recovery of carbon monoxide, nitrogen and hydrogen at a crucible temperature of 1650°C.

Sloman²⁾ pointed out that carbon in the iron bath is very reactive, and the iron metal depresses the vaporization of adsorptive elements. McDonald,³⁾ and Smith,⁴⁾ on the other hand, showed that carbon

---

1) A. L. Beach and W. G. Guldner, *Anal. Chem.*, **31**, 1722 (1959).

2) H. A. Sloman, *J. Inst. Metals*, **71**, 391 (1945).

3) R. S. McDonald, J. E. Fagel and E. W. Balis, *Anal. Chem.*, **27**, 1632 (1955).

4) W. H. Smith, *ibid.*, **27**, 1636 (1955).

becomes easily oversaturated in an iron flux at high temperature and the bath becomes very viscous, which gives erroneous low results. Smiley,[5] and Gregory[6] used platinum metal as a metal bath for the determination of oxygen in titanium, and Ogahara[7] used it for oxygen analysis in stainless steels. Platinum metal has a low vapor pressure, which minimizes the amount of metal evaporating to the furnace walls, and does not become viscous. Wilkins[8] reported that the platinum bath does not adsorb the extracted gases. Tin has been used by many investigators as a metal bath in order to eliminate the adsorption of the extracted carbon monoxide by manganese evaporated from a flux. Guldner[9] pointed out that the function of the tin in the case of addition of both iron and tin to the crucible is two-fold: first, to increase the fluidity of the bath, and second, to act as a mechanical stirrer.

A method of isotope dilution employed in the determination of gases in metals has been reported by Kirshenbaum and Grosse,[10] Pearce,[11] and Burden.[12]

An isotope dilution method using $^{18}$O-labelled carbon monoxide was employed in the present paper for the determination of oxygen in a high manganese steel without the bath technique, and with iron, platinum and tin bath techniques. When isotopic equilibrium is established only in the gas phase, this method gives results in which gas adsorption errors have been eliminated.

## Experimental

The apparatus used is identical to that reported previously.[13,14]

NBS standard steel 1041 containing 1.2% manganese was used as a sample. Specimens for each metal bath were neighboring sections cut out parallel to the aixs in order to avoid the effect of sedimentation. They were then polished with carborundum paper, rinsed in petroleum benzene, and dried in air.

$^{18}$O-labeled carbon monoxide was prepared from Hg$^{18}$O (about 90 atom%$^{18}$O), produced by the BIO·RAD Laboratory, Richmond, California, U.S.A.

**Carbon Monoxide Adsorption Curves.** After outgassing the graphite crucible, 10 g of the bath metal listed above was added and fused to be degassed at 1850°C, while metal vapor deposited continuously on the surface of the walls. A measured quantity of carbon monoxide was admitted from a storage bottle and circulated in the system. The recovery of carbon monoxide was measured. Figure 1 shows the carbon monoxide adsorption curves.

When 5 g of the sample was added to the fused metal, the carbon monoxide adsorption rate increased in platinum and in iron, while it did not change in tin. These phenomena may be related to the magnitude of the chemical affinity between the metal and carbon monoxide.

**Determination of Oxygen in NBS 1041.** The methods of isotope dilution and vacuum fusion were applied to the determination of oxygen in a sample of NBS standard steel 1041 using the above mentioned metal baths. The procedures employed were identical to those reported previously.[14]

In Table 1 are summarized these data, which are the arithmetic means of three or four determinations from outer portions of every sample rod.

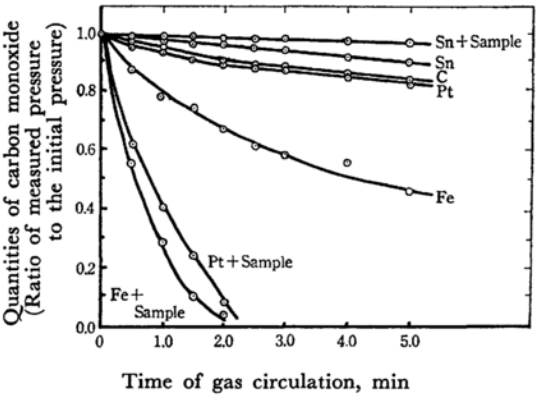

Fig. 1. Carbon monoxide adsorption curve.

TABLE 1. ANALYTICAL RESULTS OF OXYGEN IN NBS 1041

| Bath metal | — | Pt | Sn | Fe |
|---|---|---|---|---|
| Vacuum fusion method | — | 150 | 150 | 113 |
| Isotope dilution method | 163 | 214 | 159 | 223 |
| Argon fusion method | 160 | | | |
| Adsorption of carbon monoxide | very large | small | no | medium |
| $^{18}$O content in the residual gas | | close to the sample gas | diluted with $^{16}$O | close to the sample gas |

Sample: NBS 1041 Data are mean values of those from outer portions. (ppm)

---

5) W. G. Smiley, *ibid.*, **27**, 1098 (1955).

6) J. N. Gregory and D. Mapper, *Analyst*, **80**, 230 (1955).

7) I. Ogahara, W. Sekimoto and H. Matsumoto, *J. Iron & Steel Inst. Japan*, **47**, 300 (1961).

8) D. H. Wilkins and J. F. Fleisher, *Anal. Chim. Acta*, **15**, 334 (1956).

9) W. G. Guldner, *Talanta*, **8**, 191 (1961).

10) A. D. Kirshenbaum and A. V. Grosse, *Trans. Am. Soc. Metals*, **45**, 758 (1953).

11) M. L. Pearce and C. R. Masson, *Iron & Steel Inst., Spect. Rept. No.* 68, 121 (1960).

12) J. P. Burden and C. R. Masson, *J. Iron & Steel Inst.*, **202**, 28 (1964).

13) T. Somiya, S. Hirano, H. Kamada and I. Ogahara, *Talanta*, **11**, 581 (1964).

14) K. Furuya and H. Kamada, *Japan Analyst*, **15**, 1227 (1966).

When no metal bath was used, the oxygen content of the initial six specimens could not be determined owing to the large adsorption of carbon monoxide in the furnace. During 3 min of gas circulation, carbon monoxide in the system was completely adsorbed, so their isotope concentrations could not be measured. However, in the case of the final three specimens, the gas adsorption became rather small, and the isotope concentrations could be measured.

In the platinum bath method, the isotope concentration of residual gas extracted from the furnace after gas circulation was close to that of the collected gas sample. This indicates that almost all of the oxygen in the sample was already extracted from the crucible. However, there were marked differences between the results of the isotope dilution method and the vacuum fusion method caused by gas adsorption in the furnace.

In the iron bath method, the results were close to those in the case of the platinum bath in the isotope dilution method, while the results in the vacuum fusion method were lower than those in the platinum bath method. This is related both to the gas adsorption property of iron, and to the fatigue of bath action caused by carbonization viscousness. The isotope concentration of the residual gas was close to that of the collected gas sample.

In the tin bath method there were no differences between results of the isotope dilution and the vacuum fusion method. This shows that there is no gas adsorption lowering the vacuum fusion results in the tin bath method. The isotope concentration in a small quantity of the residual gas was about 90 atom% $^{16}O$, and this shows that the oxygen in the sample was incompletely decomposed and remained in the crucible.

In argon fusion analysis using no metal bath,15) the results agreed well with those obtained by the isotope dilution method with the tin bath.

The results of the isotope dilution method and the data obtained for the $^{18}O$ concentration of the residual gas indicate that the platinum and iron baths can promote reaction between carbon and oxygen in a melt. That these metal baths can partly suppress carbon monoxide adsorption is shown by a comparison of their data with the data in which no metal bath was used. The tin bath can effectively prevent the adsorption of carbon monoxide in the furnace, and does not promote the reaction in a flux.

From this consideration, though the vacuum fusion results for the platinum and tin baths are apparently in agreement, the processes of the extraction of oxygen were different from each other. In the platinum bath, part of the extracted carbon monoxide, after the promotion of the reaction by platinum, was adsorbed by the adsorptive elements such as manganese, while in the tin bath all of the incompletely extracted carbon monoxide was collected. When the metal bath technique was not used, extraction of oxygen was also incomplete.

According to the above consideration, it is desirable to use a combination bath, one containing a metal which promotes reaction in the flux, and also a metal which prevents the adsorption of carbon monoxide in the furnace. From this point of view, the mechanism of the iron-tin bath method, and the platinum-tin bath method can both be well explained.

---

15) H. Goto, S. Ikeda and A. Onuma, Rept. of Committee for the study of gaseous elements in nuclear metallic materials, No. 32, the Japan Soc. for Anal. Chem. (1963).