# COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME 16 B ANNEE 1969


# Spectrophotometric Determination of Germanium in Turkish Coals and the Modification of the Method


by

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

# Communication de la Faculté des Sciences de l'Université d'Ankara



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# Spectrophotometric Determination of Germanium in Turkish Coals and the Modification of the Method

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(Received March 20. 1969)

Since germanium is rare and is used in electronics and in medicine, it is worthwhile to search for it in various sources and study its chemistry. The main sources of it are coals and zinc ores. In the present work, a number of Turkish coals from different parts of Turkey has been analyzed for germanium and has been found a good source. Moreover the recent spectrophotometric method has been modified both by the apparatus and the procedure.

## INTRODUCTION

Germanium has a great importance in contemporary science and in industry, because of wide uses of it in electronics and in medicine. It is a grayish-white semi-metal melting at 958°C. Since the element is rare its chemistry is relatively new. It presents a great analogy to silicium and carbon.

It occurs mainly in coal in zinc ores. In some countries it is manufactured from the flue dusts and the residues, from the refining of zinc. It is percentage in coals and in ores is generally low; in some American zinc oxide ores it goes up to 0.17 % whereas the percentage of it in coals, is about 10 P. P. M.

Since germanium has proved of great interest scientific as well as industraial in modern world, it is worthwhile to search for it in natural sources. Starting from this view we have analyzed a number of Turkish coals, from different parts of Turkey, and have found a promising sample (Üzülmez bölgesi No 2). However, this work does not mean that the searches in this field are complete. We will continue to this type of work.

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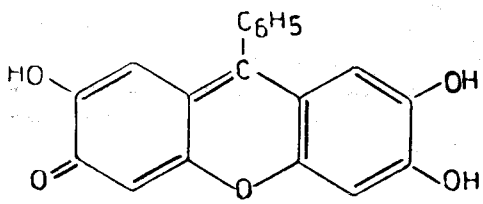
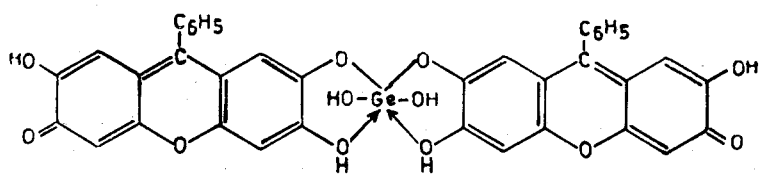
Germanium is determined by several methods. [1], [2], [3], [4], [5]. One of them is absorptiometric method. But in contrary to the other methods absorptiometric methods have not been investigated to great extent. At present two absorptiometric methods are known [4], [6]. One is based on the precipitation of germanium, as germanomolybdic acid and then reduction of molybdic acid to molybdenum blue. Since arsenic, phosphorous and silicon give the similar precipitation reactions, the method is not so useful. In the second and the more recent one germanium tetrachloride is treated with phenylfluorone (2,3,7– trihydroxy–9–phenyl–6– fluorone) to give a pink coloration. This method is about four times as sensitive as the molybdenum blue method.




The color of the solution is orange because of the mixture of the pink and yellow solutions (solution of phenylfluorone is yellow). The color of the solution increases with time and reaches to a maximum within 30 minutes, in the presence of much excess of reagent, in acidic medium (1.05 N HCl). Since the complex tends to precipitate before this time it is rendered stable by adding 0,5 percent aqueous solution of gum arabic into solution of the complex. A solution so obtained is stable for at least 14 hours. The structure of the complex is.




Pink

Cluley has shown that a few ions, such as $Sn^{+2}$, $Sn^{+4}$, $As^{+3}$ $As^{+5}$ $Sb^{+3}$, and $Fe^{+3}$ interfere with the reaction. Since germa-

nium is isolated by volatilization as tetrachloride before spectrophotometric determination is made, even the above mentioned ions are not harmful. However, some arsenic trichloride and hydrofluoric acid pass with volatile germanium tetrachloride but they do not interfere with the absorption.

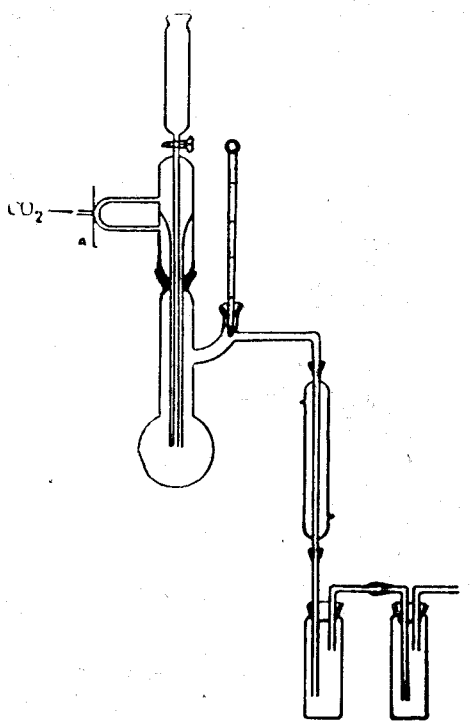



Fig – 1

In the distillation of germanium tetrachloride we have first used the apparatus Fig-1, given by Beamish and coworkers [5].

But we have noticed that this apparatus is not useful. Even, upon known samples, we could not get good results to draw a working curve. So, we have modified it. The modified form of the apparatus is seen in Fig–2. All connections of the apparatus are of ground glass joints.

Another addition to this method is that the collection, of 20 ml solution, instead of 10 ml as described by Cluley [4].

We have obtained excellent results to draw a working curve, Fig–3, after we have made these alterations. As is seen from the shape of the curve, the complex perfectly obeys the Lambert-Bouger-Beer law. By using this curve, we have determined a number of coal samles from different parts of Turkey and have got some interesting results. One of them has been found to contain as much as 0.0013 percent of germenium.

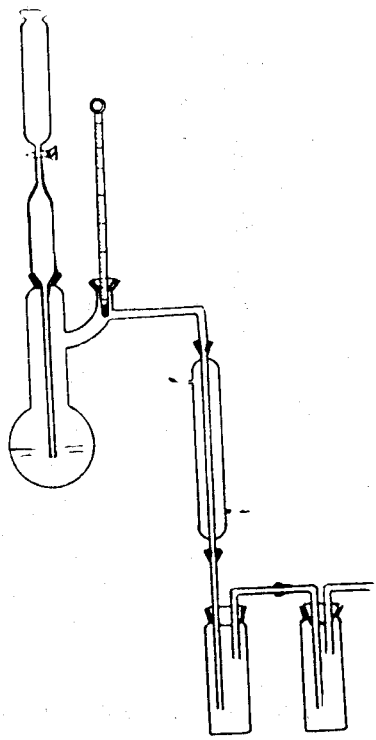


Fig – 2

The same coal contains 10 % ashes, Table–1. Experiments made upon ashes of the coal has shown no germanium at all. This means that the whole of the germanium has passed into flue dust as germanous oxide, which is stated to be volatile at 700°C [7]. So flue dust of this coal be a good and rich source for germanium.

## EXPERIMENTAL

0,5 gram of finely ground coal sample is mixed properly with 1,5 gram of dry sodium carbonate in a platinum crucible and then the mixture is covered with 0,5 gram of sodium carbonate. The crucible, containing the mixture of coal and sodium carbonate, is placed in a muffle furnace (Heraus) and the temperature is raised gradually to 600°C within an hour and heating is continued at this temperature until carbonaceous matters, at the surface have disappeared.

Then the crucible is removed from the furnace and the contents stirred carefully by a platinum wire. The crucible is placed once again to the furnace and is kept there for nearly an hour at the same temperature. In this time all the cabonaceous matters disappear once again. Finally the crucible is removed from the furnace and is heated over a good burner, such as Meker, until the last traces of the carbonaceous matters have disappeared. At last the content of the crucible is cooled and 10 ml of distilled water is added on it.

Table – 1

| No | Abs. | Ge (γ) | Ge (in 0,5g coal) | Ge % | Ash % | District |
|---|---|---|---|---|---|---|
| 1 | 0.000 | – | – | 0.000 | 10.0 | Üzülmez |
| 2 | 0.075 | 3.2 | – | – | 13.0 | Üzülmez |
| | 0.038 | 3.5 | | 0.0013 | | |
| | 0.068 | 2.9 | 6.4 (average) | | | |
| 3 | 0.022 | 0.9 | 1.8 | 0.0003 | 10.0 | Kozlu |
| 4 | 0.008 | 0.3 | 0.6 | 0.00012 | 11.3 | Gelik |
| 5 | 0.010 | 0.4 | 0.8 | 0.0001 | 13.5 | Gelik |
| 6 | 0.015 | 0.6 | | | | Üzülmez |
| | 0.018 | 0.7 | 1.3 (average) | 0.00026 | | |
| 7 | 0.013 | 0.6 | | | 13.3 | Gelik |
| | 0.021 | 0.9 | 1.5 | 0.0003 | | |
| 8 | 0.010 | 0.4 | | | 13.3 | Kozlu |
| | 0.006 | 0.3 | 0.7 | 0.00014 | | |
| 9 | 0.003 | 0.1 | 0.2 | 0.00004 | 37.9 | Kozlu İncir harmanı |
| 10 | 0.010 | 0.4 | 0.8 | 0.00016 | 16.1 | Bolu Merkez |
| 11 | 0.00 | 0.0 | 0.0 | 0.0 | 22.2 | Soma |
| 12 | 0.005 | 0.2 | 0.4 | 0.00008 | 35.7 | Çanakkale-Can Helvacı köyü Bağlarbaşı |
| 13 | 0.020 | 0.8 | 1.6 | 0.00032 | | Gediz |
| 14 | 0.015 | 0.6 | 1.2 | 0.00024 | 25.7 | Tunçbilek |

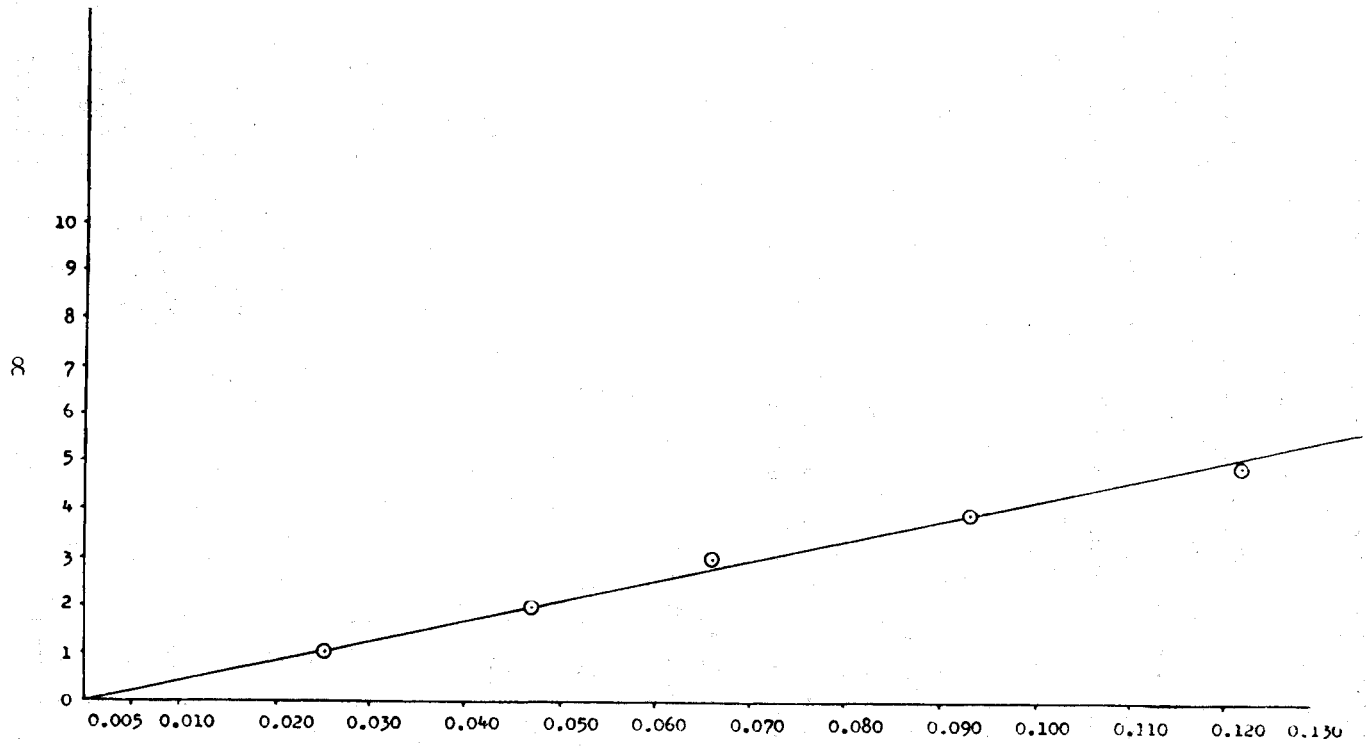

10
9
8
7
6
5
4
3
2
1
0
0.005
0.010
0.020
0.030
0.040
0.050
0.060
0.070
0.080
0.090
0.100
0.110
0.120
0.130
Absorption

Fig - 3

The contents, perfectly disintegrated with water, is transferred to the distilling flask of the apparatus Fig–2. The crucible is rinsed with 8 ml of 1:1 hydrochloric acid, and is added to the flask too. In order to liberate carbon dioxide the solution is swirled and is diluted to 25 ml. After that, 25 ml of concentrated hydrochloric acid (d = 1, 18), is added and is heated with a burner until 10 ml of distillate is collected. Then the distilling flask is cooled and is heated again until another 10 ml of distillate is collected. So, altogether 20 ml of distillate is collected. To half of the distillate in a 50 ml-graduate flask, are added 5 ml of gum arabic and 15 ml of phenylfluorone and then the solution is made up to 50 ml by distilled water.

The measurements are made at 510 m$\mu$, after 30 minutes that phenylfluorone solution has been added into the half of the distillate (for the complete developement the pink color).

The working curve has been drawn under the same conditions. Here, pure sodium germanate solution containing 10 $\mu$ germanium in one ml, has been taken instead of the coal sample.

Gum arabic solution: 0,5 gram of gum arabic is dissolved in 100 ml of the distilled water by heating.

Phenylfluorone solution: 0.030 gram of the phenylfluorone is dissolved in a mixture containing 5 ml of dilute sulphuric acid (1:6) and 85 ml of ethylalcohol by warming, then it is cooled and is made up to the 100 ml with ethylalcohol.

## Apparatus and Materials

The measurements have been made on a Beckmed DU Spectrophotometer equipped with a Beckmen DT Supply.

Germanium dioxide and phenylfluorone have been supplied from the B. D. H., sodium carbonate (pure) aud hydrochloric acid (pure) from E. Merck.

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## ÖZET

Germaniumun nadir olması, elekronik ve tıpta kullanılması dolayısıyla çeşitli kaynaklarda araştırılmasında ve nisbeten yeni olan kimyasının geliştirilmesinde faydalar vardır. Bu kaynaklar başlıca kömürler ve çinko filizleridir. Takdim edilen çalışmada Türkiyen'in çeşitli bölgelerinden gelen kömürler germanyum bakımından incelenmiş ve bunlardan birisinin oldukça ümit verici olduğu tesbit edilmiştir. Buna ilâveten bu çalışmayla şimdiye kadar kullanılmakta olan metod üzerinde de bazı değişiklikler yapılmıştır.

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Ankara Turquie.

Ankara Üniversitesi Basımevi - 1969