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Note

Electrochemical Separation of Carrier-free Iron

K. Kvastek, P. Strohal, and R. Despotović

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

Received September 30, 1966

The separation of various elements by electrodeposition using a mercury cathode has been presented in a summarised form[1]. However, as stated by Lavrukhina[2] such investigations, especially in the case of trace elements, have not been carried out systematically. Hovewer, it is well known that the deposition of iron group elements onto a Hg-cathode is followed by an overvoltage. A number of papers[3-7] present the application of this method to various systems, but a method to be applied for the separation of trace amounts of iron from large amounts of manganese using a constant potential mercury cathode system has not been described as yet.

The nature of the overvoltage effect in the case of iron deposition has not yet been clearly stated. It has been inferred that the increase of overvoltage effect of iron group elements is connected with difficulties in the crystal lattice formation, especially because *d*-levels of these atoms are not completed[8]. Popkov[5] discusses the existence of the overvoltage effect on the deposition of iron group metals in connection with an additional consumed energy needed for the deposition of metals onto a Hg-cathode. Also, it has been suggested that in this case the overvoltage is due to the consumation of a certain energy for the amalgam formation[6]. Prihodtshenkho[7] demonstrated that iron amalgam cannot be formed onto a mercury cathode if there is no current present.

Results concerning the solubility data of iron in mercury show low solubility and they are scarce and there are sometimes remarkable discrepancies[9]. Palmaer[10] described that crystals separated from a mercury cathode after electrodeposition are pure iron but not an iron-mercury mixture with a constant stoichiometric ratio. This suggests the existence of small iron crystals dispersed in mercury. These facts should therefore be taken into account when such processes are investigated. It is of interest therefore, to investigate certain parameters which may have influence on the electrodeposition of iron onto a mercury electrode. The purpose of this work was to search for the conditions under which radiochemically pure ^{55}Fe samples could be obtained.

EXPERIMENTAL

Experiments were performed in an electrode cell (Fig. 1) composed of a Pt-anode, a Hg-cathode, and a saturated calomel electrode, placed into a glass apparatus. The cell construction allows one to use volumes up to four milliliters. The analysed solutions were prepared using deuteron irradiated manganese targets. The targets were prepared by electrodeposition of manganese onto a copper holder using a manganese sulphate-ammonium sulphate-glycerine bath[10]. Deuteron irradiated manganese targets containing ^{54}Mn and ^{55}Fe activities were dissolved in a 3% H_2SO_4 solution. At the applied potentials ranging from 1200 to 1900 mV stirring was

accomplished with a stirrer. After separation the radioactivity corresponding to both fractions was measured. In some cases the ^{59}Fe activity was added to the target solution to improve the counting efficiency because ^{55}Fe decays by electron capture

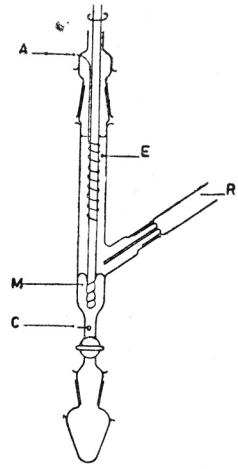

Fig. 1. Electrode cell for the separation of carrier-free iron (A — anode, C — cathode, M — mercury, E — electrolyte, R — reference electrode)

emission. The electrochemical stripping is not preferable method for removing metals from an amalgam phase because of the simultaneous removal of mercury. The removal of iron was therefore performed by means of complex formation using a 10% tartaric acid solution.

RESULTS AND DISCUSSION

Results are presented in Table 1. The manganese contamination of iron samples is shown in Fig. 2. It can be seen that under the applied experimental conditions carrier free iron samples contain less than 0.5% of manganese, even the manganese concentration in the electrolyte was as much as about 10^{10} times higher. That means that using the described procedure high purity

TABLE I

Experimental Data for the Separation

Sample No.	Cathode potential in mV	Fe contained in mercury fraction (in %)	Mn contamination (in %) of Fe containing Hg fraction
1	— 1400	18.0	0.37
2	— 1450	63.9	0.47
3	— 1500	68.0	0.56
4	— 1550	84.6	0.48
5	— 1600	79.2	0.50
6	— 1650	93.2	0.49
7	— 1700	93.4	0.42
8	— 1750	97.7	0.53
9	— 1800	99.2	59.80

carrier free iron may be obtain. Such a method can therefore be recommended for the preparation of carrier free iron samples for various applications.

Acknowledgments. The authors are indebted to Professor B. Lovreček for his interest in this work and helpful discussion.

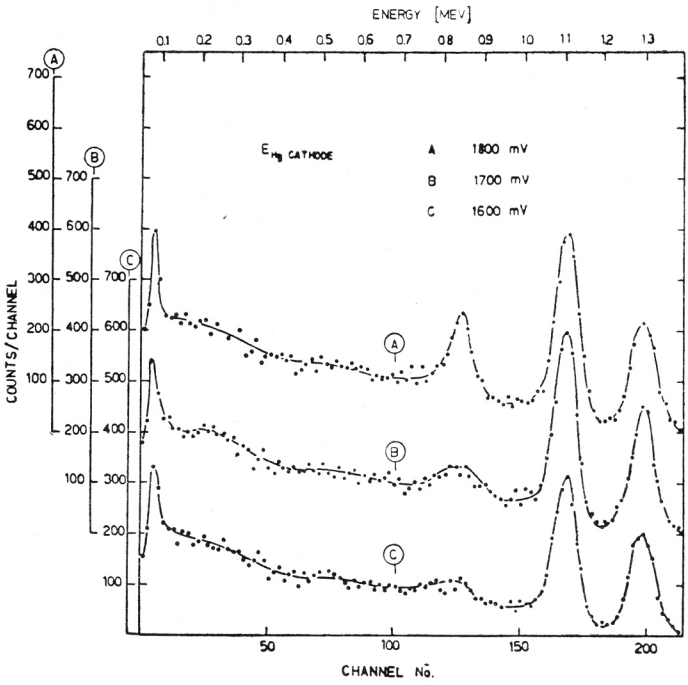

Fig. 2. Gamma ray spectra of iron samples separated under various experimental conditions. ^{54}Mn activity corresponds to 0.84 MeV.

REFERENCES

1. J. A. Page, J. A. Maxwell, and R. R. Graham, *Analyst* **87** (1962) 245.
2. A. K. Lavrukhina *Primeneniye mechenykh atomov v analyticheskoy khimii*, Akad. Nauk USSR, Moskva 1955, pp. 127—132.
3. I. Price and S. Payne, *Analyst* **74** (1949) 641.
4. I. Parks, L. Lykken, and H. Sohnson, *Anal. Chem.* **20** (1948) 148.
5. A. P. Popkov and N. L. Klimashenko, *Zh. Fiz. Khim.* **34** (1960) 1741.
6. M. T. Kozlovskii, *Zh. Prikl. Khim.* **27** (1954) 757.
7. V. G. Prihodchenko, *Zh. Prikl. Khim.* **36** (1963) 344.
8. V. P. Gladishev, *Chem. Listy* **56** (1962) 769.
9. M. Hansen, *Struktura binarnih splavov*, Tom. I., Metallurgizdat, Moskva **1950**, p. 648.
10. E. Palmaer, *Z. Electrochem.* **38** (1932) 10.
11. A. G. Gray, *Modern Electroplating*, John Wiley & Sons Inc., New York **1953**.

IZVOD

Elektrokemijska separacija željeza bez nosača

K. Kvastek, P. Strohal i R. Despotović

Ispitivana je elektrokemijska separacija željeza u radiokemijskoj formi bez nosača od gramskih količina mangana. Upotrebom izgrađene aparature, koja radi s konstantnim potencijalom živine katode, istraživani su najpovoljniji uvjeti ove separacije. Kontrola efikasnosti separacije vršena je gama-spektrometrijski. Rezultati ukazuju na mogućnost dobivanja radiokemijski vrlo čistog željeza što je od značaja kod proizvodnje radionuklida ^{55}Fe na ciklotronu.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB

Primljeno 30. rujna 1966.