

SAMPLING VOLUME OF THE *NEOCHIM* ELECTROGEOCHEMICAL METHOD

D. B. Hoover, W. D. Heran & R. W. Leinz

The poorly known CHIM electrogeochemical exploration method, a hybrid geophysical/geochemical method, is claimed by its Russian developers to be especially useful in exploration for deeply buried mineral deposits. The U.S. Geological Survey began research on the CHIM method in 1989. This research identified significant problems related to electrode design, resulting in development of an entirely new type of electrode. This new electrode now permits soil ion extractions approximating that required by Faraday's law of electrolysis. Based on a Faradaic extraction, the volume of soil sampled by a CHIM extraction is shown to be $V = m\rho Q$, where m is ionic mobility, ρ , earth resistivity, and Q , the electric charge expended. For typical CHIM operating parameters these volumes may be as much as 10^6 times the volumes of soils typically analyzed in conventional geochemical methods. It is this large difference in sample volume that provides advantages for the CHIM method.

Key words: CHIM method; Electrogeochemical exploration; Sample volume; Ion mobility.

VOLUME AMOSTRADO PELO MÉTODO ELETROGEOQUÍMICO *NEOCHIM* – *O método eletrogeoquímico CHIM é um híbrido entre técnicas de prospecção geoquímica e geofísica ainda pouco conhecido. Segundo pesquisadores russos que o desenvolveram, é especialmente indicado para a exploração de depósitos minerais profundos. O Serviço Geológico Americano (USGS) começou a pesquisá-lo em 1989, o que lhe permitiu identificar problemas importantes relacionados ao projeto original do eletrodo e desenvolver outro inteiramente novo. A nova versão permite que se faça a extração de íons do solo de uma forma mais aproximada àquela prevista para a eletrólise (lei de Faraday). Com base nesta, mostra-se que o volume de solo amostrado pela extração via CHIM é dado pela expressão $V = m\rho Q$, onde m representa a mobilidade iônica, ρ , a resistividade elétrica local, e Q , a quantidade de carga elétrica utilizada na energização. Os parâmetros operacionais, comumente empregados numa prospecção CHIM, permitem amostrar um volume de solo que pode chegar a ser um milhão de vezes maior do que o tipicamente analisado em métodos geoquímicos convencionais. É justamente nesta grande diferença entre os volumes de solo amostrado que reside a vantagem do método CHIM.*

Palavras-chave: Método CHIM; Exploração eletrogeoquímica; Volume amostrado; Mobilidade iônica.

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INTRODUCTION

The CHIM electrogeochemical technique is a hybrid geophysical/ geochemical method used to obtain samples of mobile ions directly from the soil. CHIM is an acronym derived from the Russian words "Chastichnoe Izvlechennye Metallov", meaning partial extraction of metals. The basic concept is to apply dc current to the earth through special ion collecting electrodes. With the passage of current, ions present in the earth near the electrode will migrate into an electrolyte within the collection electrodes, cations to the cathodes and anions to the anodes. In essence, it is a Faradaic extraction of soil ions.

The CHIM method was developed by researchers at Rudgeofizika in St. Petersburg about 25 years ago, and widely practiced in the former USSR (Ryss & Goldberg, 1973; Goldberg et al., 1978; Shmakin, 1985; Bloomstein, 1990).

The Russian literature states that the advantage of the CHIM method is its ability to identify geochemical anomalies over ore deposits with several hundred meters of cover, a situation where conventional geochemical methods often fail. Although principally used for base- and precious-metal exploration, it has been applied to exploration for materials as diverse as beryllium, tin, and oil and gas. Tests of the method have been conducted by the Geological Survey of India (Talapatra et al., 1986; Bose, 1987); the Peoples Republic of China has at least six groups actively researching the method (Liu et al., 1993; Luo et al., 1993; Wu et al., 1989; Xu et al., 1989). Recently, field tests have been conducted in Canada and Australia under a partnership between Rudgeofizika and Scintrex Ltd, of Concord, Canada called Geoelectrochemical Surveys Partnership (GECSP) (Ryss & Seigel, 1993).

The USGS began research on the CHIM method in 1989, basically following the Russian technology (Smith et al., 1993; Hoover et al., 1993). Our early research showed that CHIM extractions were similar to soil extractions using weak acids; geochemists refer to these as partial extractions, as opposed to complete or nearly complete dissolution of soil minerals. However, continuing research revealed significant problems with the conventional Russian technology, and showed that the applied current was not being effectively used (Leinz and Hoover, 1993). To overcome the problems identified, we redesigned the collector electrode and thus increased the

Faradaic collection efficiency from about 0.1% for the Russian type electrode to about 25% for the new design (Leinz & Hoover, 1994). We define the Faradaic collection efficiency as the ratio of the number of chemical equivalents collected to the Faradays of charge expended during a run. We believe that the ion collection process from all past CHIM studies is essentially based on ionic diffusion, rather than on ion migration under the action of an electric field, as was previously thought (Leinz & Hoover, 1993, 1994). That is, the applied current was not effectively used in these past extractions. With the new electrode design, ion extraction by migration in an electric field is the collection process and approaches an ideal Faradaic extraction. An important question now is what volume of soil can be sampled by what we call the NEOCHIM method? The advantages of NEOCHIM, we believe, are directly related to the volume of soil that can be sampled. In the following we will develop approximate measures of that volume.

CHIM SAMPLE VOLUME

For simplicity we will assume a homogeneous half-space with an electrode on the surface that is distant from any other electrode. The electrode contact surface area is also assumed small relative to the volume sampled, so that it can be considered a point source. We also assume that conduction in the earth is ionic, caused by dissociated salts present in the soil moisture. For a point source the electric potential, V , at any point in the half-space earth is given by (Keller & Frischknecht, 1966).

$$V = \frac{\rho I}{2\pi} \frac{1}{r}, \quad (1)$$

where ρ is the electrical resistivity, I is the current intensity, and r is the radial distance from the point source.

The electric field, E , at a point is obtained by differentiating Eq. (1), and is given by

$$E = \frac{-\rho I}{2\pi} \frac{1}{r^2}. \quad (2)$$

The velocity v of a particular ion is given by the product of the electric field and ionic mobility m (Joos, 1950), or

$$\frac{dr}{dt} = v = m E = -\frac{m\rho I}{2\pi} \frac{1}{r^2}. \quad (3)$$

Eq. (3) gives the net velocity of an ion due to an applied electric field at any radius, r , from the electrode as a function of the current, the earth resistivity and the mobility of that ion. Here, we do not consider the random thermal motion of the ion. Knowing the velocity as a function of distance, Eq. (3) can be integrated to give the time, t_1 , it would take for an ion to go from a point at distance r_1 to the electrode at $r = 0$. In performing this integration we are assuming a direct radial path from the point to the electrode. In the earth the path would be more tortuous, and the presence of blind pores would keep some ions from contributing to the current flow. However, this simplification permits an approximation of the travel time. Performing the integration gives

$$t_1 = \frac{2\pi}{3m\rho I} r_1^3 \quad (4)$$

This relationship was given by Jinming & Jun (1993) who noted that it would take 87 days to move ions 100 meters if the mobility $m = 278 \times 10^{-8} \text{ m}^2/\text{volt-sec}$, $\rho = 2 \times 10^3 \text{ ohm-m}$, and $I = 50 \text{ amps}$. For a 20 ohm-m earth it would take 8700 days, and even longer if the current used was a more conventional 0.5 ampere. Their point was to show that CHIM extractions as commonly practiced at currents of 0.5 amps and running for 24 hours, would not move ions over several hundred meters as suggested by Russian literature. Ryss & Goldberg (1973), in an early paper on CHIM, developed similar equations. For a uniform electric field they give:

$$t = \frac{r}{mj\rho}, \quad (5)$$

where r is the distance traveled and j is the current density. Ryss & Goldberg (1993) believed that Eq. (5) applied immediately beneath the electrode. At a greater distance they give for the travel time:

$$t = \frac{4\pi}{3mI\rho} r^3 \quad (6)$$

This relationship is equivalent to Eq. (4) except that it applies to a whole-space. Although Ryss & Goldberg (1973) developed correct equations for ion travel times early in their research, this did not discourage their belief that they could move ions over large distances. This is because they believed, based on empirical data, that ion mobilities could be thousandths to thousands of times greater than standard

dilute solution values given in most electrochemistry texts. We do not share this belief, in part because of the direct relationship between diffusivity and mobility given by the Einstein-Nernst relationship (McBain & Liu, 1931).

For univalent ions the Einstein-Nernst relationship between diffusivity, D , and anion and cation mobilities, m_a , m_c , is

$$D = \frac{2RT}{F\left(\frac{1}{m_c} + \frac{1}{m_a}\right)}, \quad (7)$$

where R is the gas constant, T is the temperature and F the Faraday.

Jinming & Jun (1993) and Ryss & Goldberg (1973) didn't proceed beyond Eq. (4) or (6). It is instructive to compute the volume of earth sampled using Eq. (4).

All ions, of the same mobility in this homogeneous half-space at distance r would arrive at time t , and of course ions at a smaller distance than r would arrive at an earlier time. The volume of the hemisphere defined by a radius r then is the volume sampled in time t . The volume, V , of this hemisphere is given by

$$V = \frac{2}{3}\pi r^3 \quad (8)$$

Substituting for r^3 from Eq. (4) gives

$$V = m\rho I t = m\rho Q, \quad (9)$$

where Q is the charge expended.

The volume is in cubic meters when resistivity, ρ , is expressed in ohm-m, mobility, m , in m^2 per volt sec, and charge Q in ampere-sec.

The volume sampled in a NEOCHIM extraction, if only one ion type is present, is simply the ion mobility times the earth resistivity times the electric charge expended. Since most ions have similar mobilities, Eq. (8) provides a good approximation of the sampling volume, and if ions of varying mobility are present then those of greater mobility will be drawn from a slightly greater volume of soil. It is also clear from Eq. (8) that for very acidic or basic soils the H^+ or OH^- ions with their high mobilities will dominate the collection process, necessitating a much larger charge expenditure to obtain other ions of direct interest.

One can obtain a different understanding of Eq. (9) by expressing the resistivity ρ in another form. The conductivity

σ , or reciprocal of resistivity, of a solution can be expressed as a function of its ionic concentration and mobility (Joos, 1950) as:

$$\frac{1}{\rho} = \sigma = \left[\sum_C \frac{n_c z_c m_c}{N} + \sum_A \frac{n_A z_A m_A}{N} \right] F, \quad (10)$$

where n is the number of each ion type, C for cation and A for anions; z is the respective valence; m is the respective mobility; N is Avogadro's number and F is the Faraday. The summations are taken over all cations and all anions present. Thus the solution conductivity is a direct function of the mole fraction (n/N) of each ion present. If, for example only potassium chloride is present in solution, Eq. (10) simplifies to

$$\sigma = \left[\frac{n_k m_k}{N} + \frac{n_{cl} m_{cl}}{N} \right] F. \quad (11)$$

The quantities $\frac{n_k F}{N}$ and $\frac{n_{cl} F}{N}$ are, respectively, the chemical equivalents per unit volume of K^+ and Cl^- ions in solution. Because the mobilities of both ions are nearly the same, Eq. (11) becomes

$$\sigma \approx \left[\frac{n_k F}{N} + \frac{n_{cl} F}{N} \right] m_k = E_{kcl} m_k, \quad (12)$$

where E_{kcl} is the number of equivalents of ionized potassium chloride per unit volume in solution.

Substituting this relation into Eq. (9) for the volume of earth sampled gives:

$$V = \frac{Q_l}{E_{kcl}}. \quad (13)$$

Thus the volume of earth sampled is the charge expended (ampere-hours) divided by the number of chemical equivalents per unit volume near the electrode. This result could have been arrived at directly from Faraday's law of electrolysis, however Eq. (9) provides a convenient means for estimating the sample volume from an earth resistivity measurement. These results are approximations because all ions present in solution within the earth may not participate in current conduction. The equivalents of potassium chloride in Eq. (12) should be understood as effective equivalents.

CONCLUSIONS

Now we can compare soil volumes sampled by NEOCHIM to volumes used in normal geochemical work. Typically a 1-gram sample, or about 0.5 cm^3 is actually analyzed in soil geochemical techniques. Fig. 1 shows NEOCHIM sample volumes computed from Eq. (9) for soil resistivities between 10 ohm-m and 10^4 ohm-m, based on mobility in dilute solution of the potassium ion of $7.62 \times 10^{-8} \text{ m}^2/\text{volt sec}$. Typical CHIM runs deliver about 0.1 Faraday to each electrode (0.5 amp for 5.33 hours). From fig. 1, for a 500 ohm-m earth, one ideally samples 0.366 m^3 , or about 10^6 times the soil volume typically used in laboratory soil analyses. It is this significantly increased sample volume, even allowing for inefficiencies, that we believe gives NEOCHIM a decided advantage over conventional soil geochemical methods.

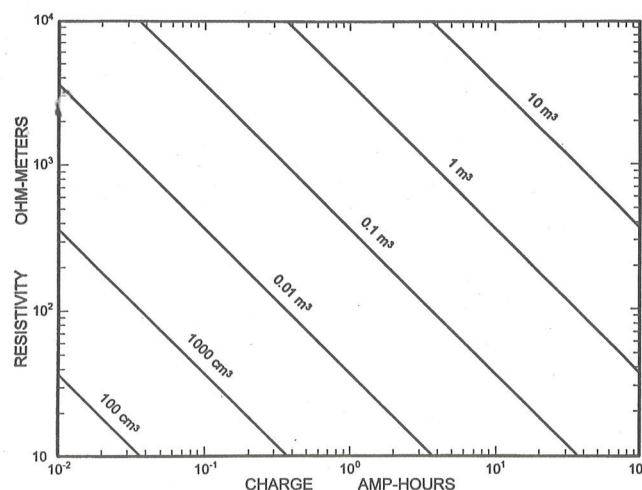


Figure 1 - Ideal soil volumes sampled by NEOCHIM extraction based on ion mobility of $7.62 \times 10^{-8} \text{ m}^2/\text{volt-sec}$ (K^+)

Figura 1 - Volume amostrado pelo método Electroquímico NEOCHIM baseado na mobilidade iônica de $7.62 \times 10^{-8} \text{ m}^2/V\text{-sec}$ (K^+)

Charge transfer	Volume (m^3)	
	20 ohm-m earth	500 ohm-m earth
Faradays		
1.0	0.147	3.667
0.1	0.0147	0.367
0.01	0.00147	0.0367
0.001	0.00015	0.0037

REFERENCES

- BLOOMSTEIN, E.** - 1990 - Selected translation of the Russian literature on the electrogeochemical sampling techniques called CHIM (Chastichnoe Izvlechennye Metallov). Introduction by D.B. Hoover & D.B. Smith: U.S. Geological Survey Open-File Report 90-462, 172 p.
- BOSE, R. N.** - 1987 - Present trend of mining geophysics in India. In 13th Annual Convention and Seminars on Exploration Geophysics, Baroda: Association of Exploration Geophysicists (India), Baroda, p. 68.
- GOLDBERG, I. S., IVANOVA, A. V., RYSS, YU. S., VEIKER, A. A., BAKHTIN, YU. G., ALEKSEEV, S. G. & YAKOVLEV, A. F.** - 1978 - Poiski i razvedka rudnykh mestorozhdeniy metodom CHIM [Investigations and research on the CHIM method in ore deposits]: Yu.I. Ryss, ed., ONTI, VTR, Leningrad, 75 p. (in Bloomstein, 1990 translation by Earth Science Translation Services, 81 p.).
- HOOVER, D. B., COOPE, J. A., LAVIN, O. P., LEINZ, R. W., NABIGHIAN, M. N., SANZALONE, R. F & SMITH, D. B.** - 1993 - The CHIM electrogeochemical sampling method-understanding the basics, problems, and application. Extended abstract SEG, SEG, AEG, U.S. Geological Survey Conference, Integrated Methods in Exploration and Discovery, Denver, Colorado, April 17-20, 1993.
- JINMING, LI, & JUN, LU** - 1993 - Theoretical and experimental study of the method of partial extraction of metals. 55th Meeting European Association of Exploration Geophysicists, abstract paper 131, 2 p.
- JOOS, GEORGE** - 1950 - Theoretical physics. Hafner, New York, 885 p.
- KELLER, G. V. & FRISCHKNECHT, F. C.** - 1966 - Electrical methods in geophysical prospecting. Pergamon Press, 523 p.
- LEINZ, R. W & HOOVER, D. B.** - 1993 - The Russian CHIM method - electrically or diffusion-driven collection of ions? *Explore* 79 (1): 5-9.
- LEINZ, R. W & HOOVER, D. B.** - 1994 - Ideal CHIM with the newly-developed NEOCHIM electrode. *Explore* 83: 10-15.
- LIU, JIMIN, LIU, ZHANYUAN & CHENG, ZHIZHONG** - 1993 - Application of electrochemical method to buried mineral exploration. 16th International Geochemical Exploration Symposium, Beijing, 11 p. (in English).
- LUO, XIANRONG, DENG, TOOSHENG, XIE, QINGLIN & YANG, XIOV** - 1993 - The study of the application of geoelectrochemical extraction technique to search for hidden ore deposits. 16th International Geochemical Exploration Symposium, Beijing, 12 p. (in English).
- MCBAIN, J. W. & LIU, T. H.** - 1931 - Diffusion of electrolytes, non-electrolytes, and colloidal electrolytes. *Chem. Eng.*, 56: 52-56.
- RYSS, YU. S. & GOLDBERG, I. S.** - 1973 - Spocob chastichnogo izvlecheniya metallov (CHIM) dlya poiskov rudnykh mestorozhdeniy [The partial extraction of metals (CHIM) method in mineral exploration]: in Metodika i Tekhnika Razvedki, ONTI, VITR, Leningrad, 84: 5-19 (in Bloomstein, 1990 translation by Earth Science Translation Services of section entitled *CHIM surface set-up for unipolar extraction*).
- RYSS, YU. S. & SEIGEL, H. O.** - 1993 - Some results of applying Russian geoelectrochemical methods in Canada: Scintrex Ltd., Concord, Ontario, Canada, 16 p.
- SHMAKIN, B. M.** - 1985 - The method of partial extraction of metals in a constant current electrical field for geochemical exploration. *Journal of Geochemical Exploration*, 23: 27-33.
- SMITH, D. B., HOOVER, D. B., & SANZALONE, R. F.** - 1993 - Preliminary studies of the CHIM electrogeochemical method at the Kokomo Mine, Russell Gulch, Colorado. *Journal of Geochemical Exploration*, 46: 257-278.
- TALAPATRA, A. K., TALUKDAR, R. C. & DE, P. K.** - 1986 - Electrochemical technique for exploration of base-metal sulphides. *Journal of Geochemical Exploration*, 25: 389-396.
- WU, ZHONGUA, JIN, YANGFE & HUANG, HONGKU** - 1989 - Gold concentration from well water by the hydroelectrical extraction method. *Journal of Geochemical Exploration*, 33: 247-254.
- XU, BANGHIANG, FEI, XIQUAN & WANG, HEPING** - 1989 - Electrogeochemical extraction technique in the prospecting of buried gold deposits. *Journal of Geochemical Exploration*, 33: 99-108.

Submetido em: 13/10/94

Revisado pelo(s) autor(es) em: 25/05/95

Aceito em: 10/06/95

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