Overview on the Electrogeochemical Techniques

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INTRODUCTION

Electrogeochemistry is an aspect of applied science combining concepts and techniques originally developed in geology, geochemistry, geophysics and electrochemistry; these techniques have been particularly adapted to specific tasks in the following sectors: mineral exploration, mineral deposit evaluation, mining environment monitoring.

The scope of electrogeochemistry includes some well-known geophysical techniques such as the spontaneous polarisation (SP) and the induced polarisation (IP) methods. In this presentation we will be concerned only with a number of other techniques not regularly used in Western exploration practice. These latter techniques were developed in the period from the 1960s to the early 1990s mainly by research and development teams in the St-Petersburg's area of Russia (VIRG, Rudgeofizika, SPSMI, SPSU) [see the list of abbreviations] following preliminary research work done from the late 1940s to the 1960s on the spontaneous electrochemical processes taking place in the immediate vicinity of metallic sulphide deposits.

Contrary to most geophysical techniques, the electrogeochemical techniques developed in this context provide information related to the *composition* (mineral-wise or element-wise) of the target investigated from a remote location. The use of these techniques has been restricted mainly to projects located in the former Soviet Union (FSU) and in China until the 1980s but more recently tests of some of these techniques have been carried out in Australia, Canada, India, USA, etc. As they provide information about the composition of the target, these techniques are classified as *direct* methods while most geophysical techniques provide information about physical property contrasts such as magnetic, density, electric resistivity or seismic velocity and are regarded as *indirect* methods.

OVERVIEW

The electrogeochemical methods originally developed in the St-Petersburg area may be grouped in two categories. In the first category are procedures based on the *selective* determination of components that have undergone some form of vertical migration from deep seated ore deposits; these techniques have been used both at the regional and at the detailed exploration stages. In the second group, we have several techniques based on the *electrochemical polarisation properties* of in-situ materials and in particular of ore minerals; these techniques have been used at the detailed exploration and evaluation stages and also as a monitoring tool during mining.

FIRST GROUP OF TECHNIQUES

The techniques in the first category includes the MPF, TMGM, CHIM and MDI techniques. The first two (MPF and TMGM) are concerned, respectively, with the extraction of trace elements trapped in the soils' humate-fulvate complexes (organic compounds found in soils) and in secondary iron and manganese oxides. They were designed as relatively low cost methods for regional exploration, i.e. in a typical exploration project, samples are collected at large sampling intervals; also, up to 1987, ten times more MPF analyses were undertaken than TMGM probably reflecting the approximate relative costs of each of these techniques. The CHIM and MDI techniques, on the other hand, were designed as detailed investigation techniques involving a much smaller number of samples at a smaller sample interval (typically less than 60 meters) but at a higher cost per sample. While the MPF and TMGM may be classified as passive methods since a sample of in-situ material is collected in a specific soil horizon in a single step, the CHIM and MDI have an active component.

In the CHIM method, a local electric field is set-up through the sampling device (also called 'element receiver'; this device contains an electrode) in the surrounding area enhancing the migration of specific ions to the 'receiver'. In the MDI method, however, this process is enhanced only by localised diffusion: an acid solution is put in contact with the soil through a semi-permeable membrane which triggers ions migration to the 'receiver' by an osmosis-like process. In both cases (CHIM and MDI) the content of the collected sample is time dependent; the optimum time often being in the order of 24 hours which require two visits at each sampling site. The analysis of the collected MDI and especially CHIM samples currently requires the use of the ICP-MS technique for the analysis of some of the collected elements.

The MDI technique has some advantages over the CHIM technique: first it does not require the set-up of an electric current generator/controller made-up of a whole array of current sources, link cables and a remote auxiliary electrode as used in the CHIM technique and second

the concentrations of elements are significantly higher in a sample collected through the MDI technique. From the Russian experience with both the CHIM and MDI techniques, it has been observed that the results from the CHIM method show a narrower pattern, which is more closely centred on the locations on the ground surface, corresponding to the vertical projection of the deep mineralised body. Therefore, for exploration borehole siting, it appears that the CHIM results provide a more accurate position of the mineralised source.

Results obtained with these techniques include instances of indications of mineralisation in areas of thick overburden; some of the observed anomaly patterns, observed with this first group of electrogeochemical techniques, are different from the dispersion patterns
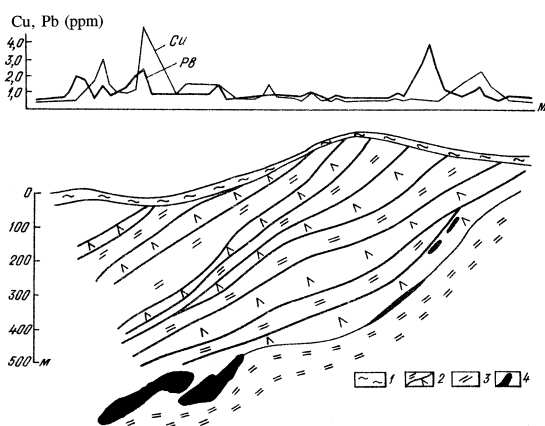
Figure 1: *Results of an MDI survey on the Maleevski deposit (Duxhanin, 1989). 1: loam; 2: basic rocks; 3: calcareous-siliceous and siliceous siltstones; 4: ore deposits.*
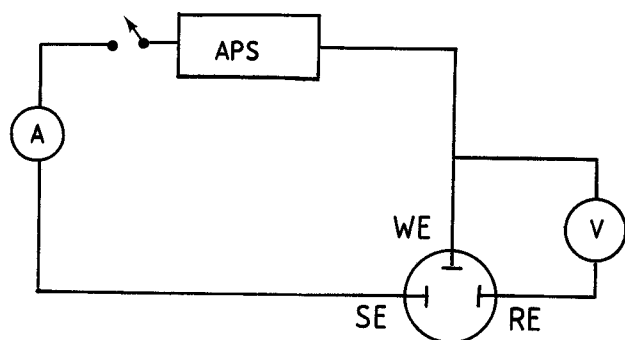
Figure 2: *Three-electrode electrolysis cell (after Ryley and Watson, 1987). WE: working electrode; SE: secondary electrode; RE: reference electrode; V: high input impedance voltmeter; A: galvanometer; APS: adjustable DC power supply.*

expected from deep sources below a considerable thickness of barren material. Figure 1 is an example, extracted from the Russian literature (Duxhanin, 1989), of an MDI profile over a mineralised body with minimal lateral displacement of the anomalous Cu-Pb pattern below several hundred meters of barren material, where the expected dispersion pattern may be laterally displaced due to the dipping structure and the anomaly amplitude may be smaller and the pattern more gradual due to the thickness of the cover.

TECHNIQUES OF THE SECOND GROUP

In the second category of techniques i.e. those based on the electrochemical polarisation properties of in-situ materials, the main techniques developed were the CPC, CLPC and the PL techniques. These are all voltammetric methods, somewhat similar to the polarography technique used in analytical chemistry for the determination of metallic compounds. In these techniques, an electric current is used to produce an electrochemical reaction. The basic configuration is illustrated with Figure 2: in a *laboratory environment* the 3 electrodes cell shown in the schematic diagram are easily identified:

- The *working electrode* (WE) is normally built with the smaller active area to have higher current density; the electrochemical reaction is taking place at this electrode; in polarography the working electrode is a dropping mercury electrode (DME).

- The *secondary electrode* (SE) (also called auxiliary or current return electrode) is used to close the current circuit and usually has a larger area.

- The *reference electrode* (RE) is not part of the current circuit; it is used for the measurement of the electric potential at which the electrochemical reaction is taking place at the working electrode together with a high input impedance voltmeter.
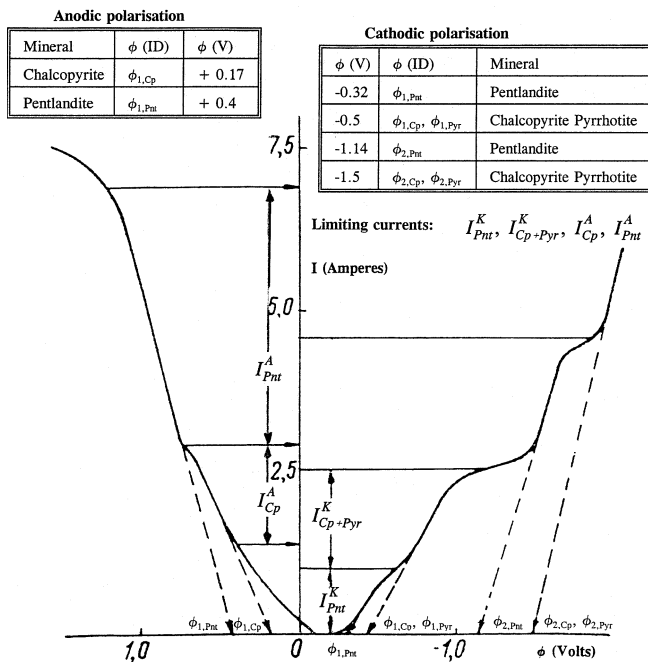
A typical data set is displayed as a *voltammogram* or *polarisation curve* (PC) which is an X-Y diagram where the X-axis normally represent the electric potential while the Y-axis may represent the electric current or the electric current density according to the context. The measure of the potential difference, after appropriate processing, leads to the identification of the particular electrochemical reaction taking place while the measure of the current, also after suitable processing, leads to an estimate of the quantity of material involved in the reaction: in a laboratory system this usually provides the concentration of the reacting component.

During the development of the electrogeochemical methods, this technology has been adapted to make in-situ measurements either on ore deposits, to find out their composition and mineral content, or as a borehole logging tool, to monitor the composition of borehole water in-situ.

CPC technique — The first of these voltammetric techniques is the CPC (or Contact mode of Polarisation Curves) and it is used for the direct in-situ analysis of a whole deposit, provided this deposit has electronic conduction (which is the case for all the common metallic sulphide deposits having a high enough sulphide content and an internal texture allowing electrical continuity). The CPC technique uses the mineral deposit itself as the working electrode through an intersecting borehole; it also uses a reference electrode (often a calomel reference electrode adapted to field conditions) on the surface at a nearby location while the auxiliary 'current return' electrode is installed at a remote location. Figure 3, after Ryss (1971), summarises this layout. The technique provides information on the composition, tonnage and, in favourable
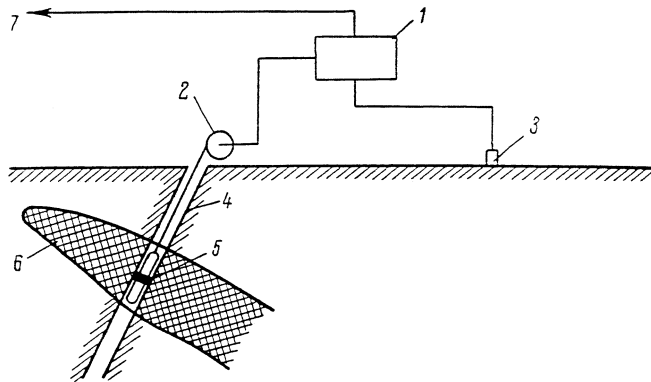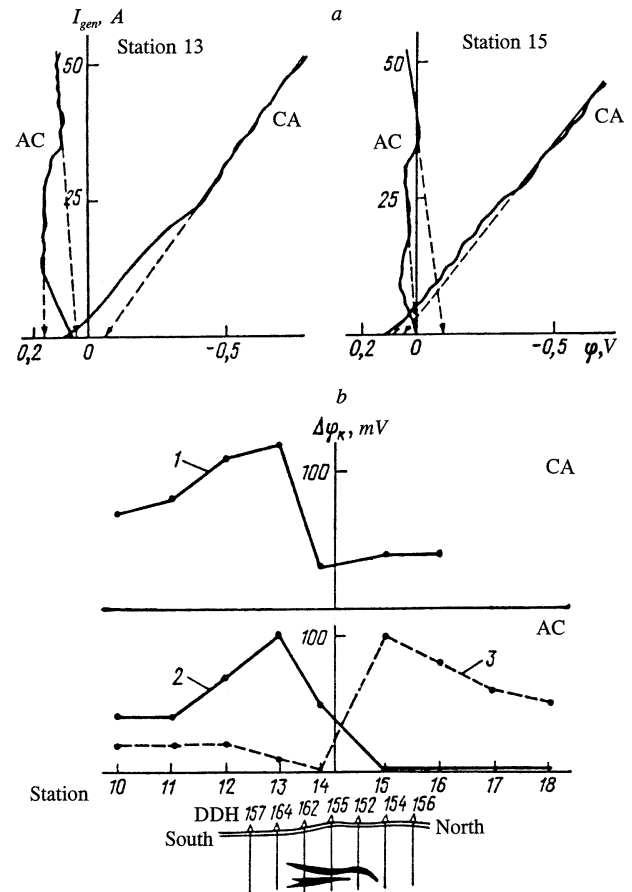
Figure 3: *Schematic diagram for the field implementation of the CPC technique (Ryss, 1971) 1: CPC control and measuring unit; 2: borehole logging cable winch; 3: RE: reference electrode; 4: borehole; 5: ore contacting tool; 6: ore deposit (WE: working electrode); 7: SE: remotely located secondary electrode.*

Anodic polarisation

Mineral	ϕ (ID)	ϕ (V)
Chalcopyrite	$\phi_{1,Cp}$	+ 0.17
Pentlandite	$\phi_{1,Pnt}$	+ 0.4

Cathodic polarisation

ϕ (V)	ϕ (ID)	Mineral
-0.32	$\phi_{1,Pnt}$	Pentlandite
-0.5	$\phi_{1,Cp}, \phi_{1,Pyr}$	Chalcopyrite Pyrrhotite
-1.14	$\phi_{2,Pnt}$	Pentlandite
-1.5	$\phi_{2,Cp}, \phi_{2,Pyr}$	Chalcopyrite Pyrrhotite

Limiting currents: $I_{Pnt}^{K}, I_{Cp+Pyr}^{K}, I_{Cp}^{A}, I_{Pnt}^{A}$

Figure 4: *Polarisation curve recorded over a copper-nickel mineral deposit. (Ryss, 1973) ϕ: electrochemical potential (volts); I: current (amperes).*

Figure 5: *CLPC results on a subhorizontal polymetallic ore deposit. (Ryss, 1983) (a) Anodic-cathodic (AC) and cathodic-anodic (CA) polarisation curves for stations 13 and 15 of the profile passing through the boreholes 155 and 156. (b) Curves of $\Delta\phi_k$ along the profile passing through the boreholes 155 and 156 for the second order cathodic (1) and second order anodic (2) electrochemical reaction on the southern part of the ore-body and for the second order cathodic electrochemical reaction on the northern part of the orebody (3).*

cases, zonation within a given deposit. Figure 4 (Ryss, 1973) illustrates a CPC data set acquired in Russia, where the diagonal dotted lines point to the reaction's potentials which are used to identify the electrochemical reaction involved and therefore the mineral investigated, while the horizontal lines indicate the changes of current related to a particular electrochemical reaction; these are used to quantify the content of each main mineral. In this particular case, the main minerals detected were chalcopyrite, pentlandite and pyrrhotite. The CPC technique makes use of
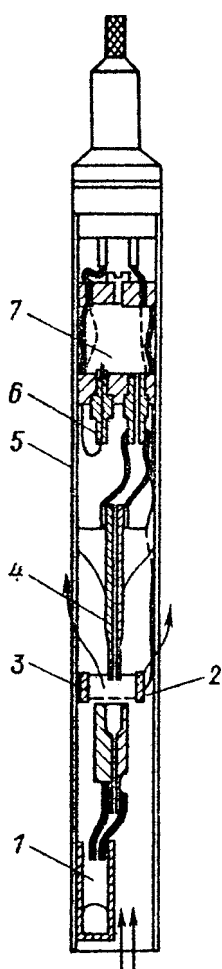
information acquired through both polarities of excitation current, i.e., both anodic and cathodic. The convention used in this voltammogram is the display of the electrochemical potentials with negative values to the right (as usual in electrochemistry) and to consider the absolute value of the current with the positive direction to the top. In Figure 4, $\phi_{1,Cp}$ is the value corresponding to a specific electrochemical reaction: the subscripted indicator refers to the order of the reaction and the mineral involved (here *Pnt* is pentlandite, *Cp* is chalcopyrite and *Pyr* is pyrrhotite). Similarly, *I* is the value of the limiting current with the superscript character indicating an anodic (*A*) or cathodic (*K*) reaction while the subscripted indicator in this case refer to the identity of the mineral(s) involved as before. The estimated mass of each mineral in this small lens was evaluated as follows: chalcopyrite: $\sim$0.67$\cdot$10^6 kg, pentlandite: $\sim$1.3$\cdot$10^6 kg and pyrrhotite: $\sim$2.5$\cdot$10^6 kg. The method has the following potential advantages: (1) detection of a main ore mineral
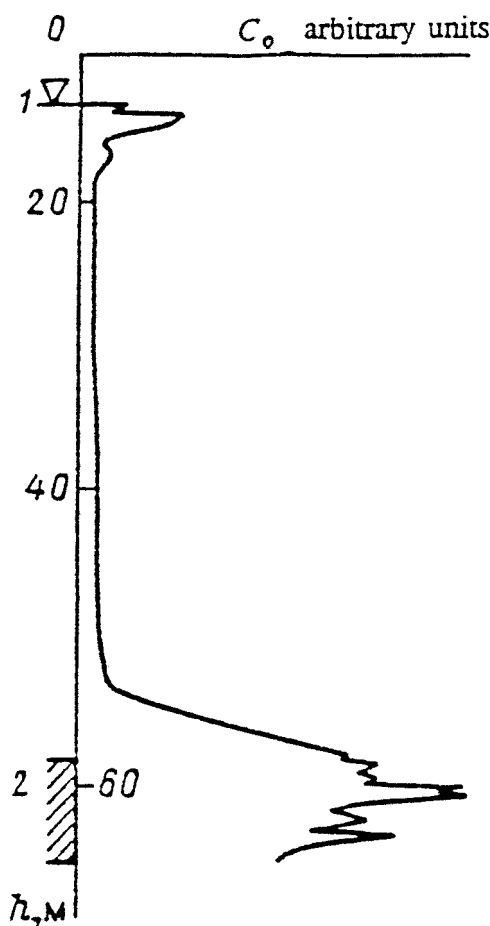
not yet intersected by a borehole (for example in the case of a deposit with definite minerals zonation pattern when one of the zones has not yet been intersected by a borehole ie the borehole may have intersected only galena but the deposit also contains a sphalerite-rich zone), (2) evaluation of an entire deposit to have a rapid but approximate estimate of its value, (3) evaluation of a deposit to a predetermined level of accuracy but with a smaller number of boreholes than what is required with a technique relying only on boreholes' mineralisation intersections.

CLPC technique—Considering next the CLPC technique, it is an extension of the CPC for the cases where an intersection is not yet available i.e. prior to drilling a conductive anomaly; it is called the Contact-Less method of Polarisation Curves and in this technique all the electrodes are located on surface. The technique will only provide composition information from the part of the target closest to the surface; it

is the least well known of the listed methods. In this case there is no direct contact with the ore deposit; instead a very high electric field is set-up in the ground above a conductive deposit and the combined response of the surrounding host materials and the conductive deposit is measured. After appropriate compensation for the host media, the response from the deposit is determined and analyzed. This CLPC technique has depth limitations and its accuracy is a function of several empirically determined variables. Figure 5 (Ryss, 1983) illustrates a CLPC test data acquired by a Russian team over a deposit where drilling information was available; the CLPC survey data was acquired using only electrodes located on the ground surface. Due to the geometry of the field excitation, one part of the target undergoes an anodic excitation while the opposite end goes through a cathodic excitation (following some orientation conventions such a cycle would be called an anodic-cathodic [AC] cycle; reversing the polarity of the excitation will produce a cathodic-anodic [CA] cycle; see Figure 5). After processing, which is more involved than in the case of CPC data, the CLCP data interpretation provided the Cu and Zn content of the deposit under investigation; in this particular case the Cu content was 15% less than the value deter-

Figure 6: *Schematic diagram for the polarographic logging tool. (Putikov, 1987) 1: receptacle for the spent mercury; 2 & 6: pressure-sealed electric contacts; 3: SE: secondary electrode; 4: WE: working electrode (dropping mercury electrode); 5: protective housing; 7: pressure compensation and isolation device.*

Figure 7: *Continuous polarographic logging record for the determination of the dissolved oxygen concentration, Northern Tadjikistan. (Putikov, 1993) 1: water level; 2: screen interval.*

mined with the boreholes' mineralisation intersection while the Zn content was 2.5 times larger than the one determined by the borehole's mineralisation intersections; it must be remembered, however, that this last technique, contrary to the CPC, does not investigate a whole deposit but only a part nearest to the surface.

Polarographic logging—Finally, the PL or Polarographic Logging is an adaptation of the polarography technique to the borehole environment and allows real-time continuous or discrete station analysis of a borehole's water composition: a borehole log is made which displays the concentration of specific ions as a function of depth. In this case, the electrolytic cell is as small as a laboratory cell but it is compensated for the hydraulic pressure in the water column. Figure 6 (Putikov, 1987) illustrates the main components of the logging tool, while Figure 7 (Putikov, 1993) is a continuous log of the concentration of oxygen in a borehole in Northern Tadjikistan. Although this log is in arbitrary units, the PL technique is also used with a calibration in mg/l. In the illustrated case, the log was run to determine the position of screen for water extraction but it has also been used to monitor the composition of groundwater during leach mining and near intensive industrial agriculture operations.

The poster will provide a brief description of each of these techniques and a selection of survey results both from areas within the FSU and from other locations.

Abbreviations:

CHIM	Method of partial metal extraction
CLPC	Contactless mode of polarisation curves
CPC	Contact mode of polarisation curves
DME	Dropping mercury electrode
FSU	Former Soviet Union
ICP MS	Induced coupled plasma spectrometric analysis with mass spectroscopy
MDI	Method of diffusion extraction
MPF	Method of extraction of element occurring within humate-fulvate complexes of soils
PC	Polarisation curve or: voltammogram, *i-E* curve, *j*-η curve etc. in polarography
PL	Polarographic logging
Rudgeofizika	Russian state mining exploration enterprise
SPSMI	St-Petersburg State Mining Institute
SPSU	St-Petersburg State University
TMGM	Thermo-magnetic extraction of metals adsorbed by secondary iron and manganese oxides
VIRG	Russian State Research Institute on Exploration Method

REFERENCES

Duxhanin, A.S., 1989, Use of the MDI technique for the exploration of deep-lying deposits; *in* Methods of exploration geophysics, Rudgeofizika, Leningrad, 99-109 (in Russian).

Putikov, O.F., 1987, Basic theory of the geoelectrochemical methods of exploration; Leningrad University Press (in Russian).

Putikov, O.F., 1993, Geoelectrochemical methods of exploration and evaluation, Textbook; SPSMI Press, Leningrad (in Russian).

Ryley, T. and Watson, A., 1987, Polarography and other voltammetric methods; John Wiley & Sons.

Ryss, Yu. S., 1971, Contact mode of polarisation curves; in Borehole mining geophysics, G.K. Volosyuk and N.I. Safronov, eds., NEDRA, Leningrad, 322-372 (in Russian).

Ryss, Yu. S., 1973, Exploration and evaluation of ore deposits by the contact mode of polarisation curves; NEDRA, Leningrad (in Russian).