

Abrasive stripping voltammetry – the electrochemical spectroscopy for solid state: application for mineral analysis

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**„Abrasive Stripping Voltammetry“ –
 eine elektrochemische Spektroskopie für Festkörper:
 Anwendung auf Mineralidentifizierungen**

Summary. Abrasive stripping voltammetry possesses several features of a spectroscopy. It allows the qualitative and quantitative analysis of electroactive solid materials. This work is focussed on the application for the unambiguous identification of minerals (sulphides, sulfo-salt minerals, fahlores). µg-amounts of a mineral are sufficient to perform a series of measurements. Three different voltammetric modes were used to study the electrochemical behaviour of the minerals.

Introduction

The fast and reliable identification of minerals is of the utmost importance not only for the mineralogist. Though this is possible simply by visual examination in the case of many minerals, it is impossible for an even larger number of other minerals. Often, the mineralogist faces problems associated with the formation of mixed crystals and impurities so that the success of identification procedures depends on the applied analytical method. The mineralogist applies in today's practice several instrumental methods, X-ray diffraction being the most important one, due to its accessibility and information yield. The development of modern electronic devices necessitated the origin of many methods for solid state and surface analysis [1–3] which can be successfully applied for mineralogical problems as well. To name but a few of these methods one should mention: secondary ion mass spectrometry (SIMS), neutron activation analysis (NAA), total-reflection X-ray fluorescence (TXRF), laser microprobe analysis (LMA) [4]. These methods are highly useful to identify minerals, in some cases even when they are of microscopic size. On the other hand, every analytical method has its inherent limitations. Not to speak about the price of equipment and the sometimes cumbersome pro-

cedures of sample preparation. Another important aspect is the possibility to build battery driven field instruments, which are desirable for field work.

Electrochemical analysis has a long tradition in application for mineral and ore analysis. Electrogravimetry [5] and polarography [6] were applied after dissolving the minerals in an appropriate way. So-called electrography [7] was utilized for direct imaging of minerals (e.g., nickeline) in rocks. This may be achieved by covering a polished rock section with a filter paper wetted with dimethylglyoxime solution and pressing a metallic plate as the cathode against the opposite site of the paper. Then electric contact is made toward the rock (e.g., nickeline being a semiconductor) and the metal plate. The nickeline is anodically oxidized giving rise to the formation of the red nickel-DMG complex on the filter paper and thus producing a “negative” image of the nickel distribution in the rock. Electrography, erst-while highly recommended, is very seldom used today [8] since its applicability is limited and the information yield rather poor compared with modern instrumental methods. But the direct electrochemical analysis of solid materials was always a great challenge. The most successful attempts were made by Brainina et al. and some other Soviet research groups [9, 10]. Since the direct use of e.g., an alloy as the electrode is accompanied by several drawbacks (severe electrode manufacturing, high currents, impossibility of satisfactorily measuring the anodic dissolution of different constituents) the solid material was usually diluted with an inert substance to make either a graphite paste electrode with an admixture of the electroactive component or to press tablets. These are cumbersome procedures, in their inconvenience surpassed only recently [11] when the solid material (pyrite) was solubilized with the help of a detergent (styrene-cationic surfactant-water emulsion with finely powdered pyrite). The styrene polymerizes on the electrode surface (Pt) and binds the detergent and pyrite. Doubtless, all these attempts are not satisfactory for any routine. So, asking, what are the possibilities electroanalysis can offer for solid state and hence mineral analysis, one is tempted to answer not much. But recent developments in this laboratory changed the situation. A very easy technique – the so-called abrasive stripping voltammetry – was introduced to perform qualitative and quantitative analysis of solid materials [12–15]. The analysis of lead-antimony and tin-bismuth alloys was per-

formed with this new method. Here, we report identification procedures for the following minerals:

zinkenite $\text{Pb}_9\text{Sb}_{22}\text{S}_{42}$,
 plagionite $\text{Pb}_5\text{Sb}_8\text{S}_{17}$,
 boulangerite $\text{Pb}_5\text{Sb}_4\text{S}_{11}$
 dadsonite $\text{Pb}_{10+x}\text{Sb}_{14-x}\text{S}_{31-x}\text{Cl}_x$,
 antimonite Sb_2S_3 ,
 ramdohrite $\text{Ag}_3\text{Pb}_6\text{Sb}_{11}\text{S}_{24}$,
 krockite PbCrO_4 ,
 semseyite $\text{Pb}_9\text{Sb}_8\text{S}_{21}$,
 jamesonite $\text{Pb}_4\text{FeSb}_6\text{S}_{14}$,
 heteromorphite $\text{Pb}_7\text{Sb}_8\text{S}_{19}$,
 galenite PbS ,
 andorite $\text{PbAgSb}_3\text{S}_6$,
 and cinnabar HgS .

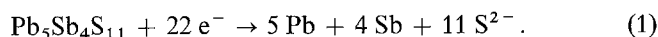
The sulfo-salt minerals constitute a large group of ore minerals [16]. They are commonly associated with rich ores of silver, copper, lead, and antimony and they are important indicators for the history of minerals and deposits. The knowledge of their thermochemistry is still relative small [17] due to extreme difficulties in performing the synthesis. Whether the extraction of thermodynamic data with the help of measurements as described here will be possible or not depends on the reversibility of the electrode processes. At least, in principle the method of abrasive stripping voltammetry has these potentials. Thus studies of the electrochemistry of minerals, as may be performed by the method of abrasive stripping analysis, should yield information about the genesis of minerals and deposits.

The aim of this paper is to point out, how fast, reliable, and easy minerals can be identified with the electrochemical solid-state analytical technique of abrasive stripping voltammetry.

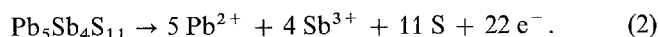
The technique of abrasive stripping voltammetry

The technique of abrasive stripping voltammetry has been described recently in this journal [12]. Therefore, only a brief description of the main feature will be given here. The idea is to transfer trace amounts of the solid material by abrasion from the latter onto the surface of a solid electrode [e. g., a paraffine impregnated graphite electrode (PIGE)]. These traces can undergo several different electrochemical reactions when the PIGE is introduced into an usual electrochemical cell with an auxiliary and reference electrode and an electrolyte solution. The electrochemical reactions can easily be traced with the help of differential pulse voltammetry. In the case of sulfo-salt minerals the following modes were applied:

1. Cathodic scan with differential pulse voltammetry, monitoring the reaction (e. g., in case of boulangerite):



2. Anodic scan with differential pulse voltammetry, monitoring the reaction:



3. Preliminary electrochemical reduction according to reaction (1) followed by an anodic scan with differential pulse voltammetry, monitoring the reactions:



This can easily be performed using a program for the conventional stripping voltammetry, as it is available in connection with all modern instrumentation. Obviously, the latter mode should be especially valuable, since it reveals

information on the qualitative (elemental) and quantitative composition of the minerals.

An important result of the investigations with abrasive stripping voltammetry is that electrochemical solid-state reactions, of course with the participation of the solution, but not necessarily proceeding via dissolved ions can be studied.

The new technique possesses the features of a spectroscopy, since the voltammograms are genuine fingerprints of the solid material, allowing a qualitative and quantitative analysis.

Experimental

The equipment and the general procedure of abrasive stripping voltammetry have been described elsewhere [12]. Preliminary experiments gave the result that the following electrolytes of mixtures of oxalic acid and sodium hydroxide are very useful for the analysis of sulfo-salt minerals:

	0.1 mol/l oxalic acid	0.1 mol/l sodium hydroxid	pH
	[vol-%]	[vol-%]	
Cathodic scan	33	67	5.0
Anodic scan	100	—	1.3
Anodic scan after preliminary reduction	57	43	2.0

Table 1 summarizes all studied minerals indicating the chemical composition and origin. All samples were preliminarily identified by X-ray diffraction (F. Damaschun).

A sample amount of about 500 μg was put on a glazed porcelain plate with a relative rough surface and the paraffine impregnated graphite electrode was gently rubbed on it, so that the mineral was crushed and ground and some traces were transferred onto the electrode surface. According to the currents the transferred amounts are in the 10^{-8} g range. The electrode can be cleaned by rubbing it vigorously on filter paper. The amount of 500 μg , once crushed and ground, is sufficient for several analysis.

Results and Discussion

Figure 1 depicts the cathodic differential pulse voltammograms of several sulfo-salt minerals including galenite and antimonite. Obviously, the difference in the shape of the voltammograms are not very pronounced. The only exceptions being dadsonite and antimonite, which both may be unambiguously identified. It should be born in mind that the different intensity of the peak is solely dependent on the amount of mineral transferred onto the electrode. It is the relation between two or more peaks of one voltammogram which can be used as a criterion for identification. Beside these relations the peak potentials and the peak shape are indispensable for the exact classification. The voltammograms of Fig. 1 reveal that there are only slight differences in the cathodic reduction of these minerals. In the case of galenite the dependence of the reduction peak potential on pH was studied (Fig. 2), giving the expected

Table 1
Compilation of studied
minerals

Sample	Mineral	Chemical compound [18]	Locality
A	Galenite	PbS	Neudorf, Harz, GDR
B	Dadsonite	$Pb_{10+x}Sb_{14-x}S_{31-x}Cl_x$	Wolfsberg, Harz, GDR
C	Boulangerite	$Pb_5Sb_4S_{11}$	Neumühle, Thur., GDR
D	Jamesonite	$Pb_4FeSb_6S_{14}$	Hartmannsdorf, Sax., GDR
E ₁	Heteromorphite	$Pb_7Sb_8S_{19}$	Arnsberg, Westf., FRG
E ₂	Heteromorphite	$Pb_7Sb_8S_{19}$	Wolfsberg, Harz, GDR
F ₁	Semseyite	$Pb_9Sb_8S_{21}$	Mine d'Anglais, Haute Loire, France
F ₂	Semseyite	$Pb_9Sb_8S_{21}$	Neumühle, Thur., GDR
G	Plagionite	$Pb_5Sb_8S_{17}$	Wolfsberg, Harz, GDR
H ₁	Zinkenite	$Pb_9Sb_{22}S_{42}$	Neumühle, Thur., GDR
H ₂	Zinkenite	$Pb_9Sb_{22}S_{42}$	Wolfsberg, Harz, GDR
I	Antimonite	Sb_2S_3	Neumühle, Thur., GDR
J	Andorite	$PbAgSb_3S_6$	Itos Mine, near Potosi, Bolivia
K	Ramdohrite	$Ag_3Pb_6Sb_{11}S_{24}$	Chokaya, near Oruro, Bolivia

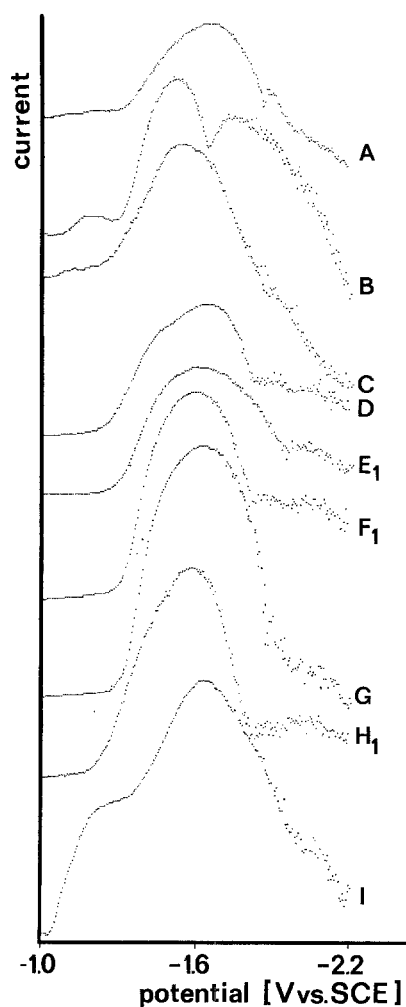


Fig. 1. Abrasive stripping voltammograms (cathodic differential pulse mode) of different minerals. See Table 1 for the denotation and Table 2 for the exact values of the peak potentials

result that the peak potential shifts 25.8 mV/pH below $pK_{a1}(H_2S)$ and 61.3 mV/pH above $pK_{a1}(H_2S)$, which is close to the theoretical value of 29.58 mV/pH and 59.16 mV/pH resp. (25°C). The deviation of the plot E_p -pH from linearity above $pH \approx 10$ should be due to the formation of hydroxo

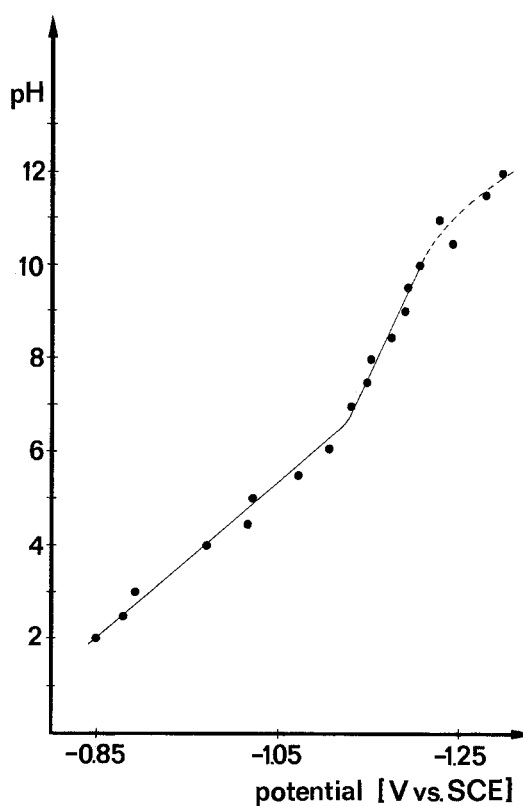


Fig. 2. Dependence of the peak potential of the PbS reduction on pH

complexes of lead. Thus Fig. 2 is in full accordance with the assumption of a reduction yielding lead and S^{2-} -ions. The peak potentials of the cathodic scans are summarized in Table 2.

More pronounced differences in the voltammetric behaviour of the minerals can be observed when the anodic differential pulse voltammograms (Fig. 3) are recorded. It is somewhat surprising that the anodic oxidation ($S^{2-} \rightarrow S + 2e^-$) is a much more characteristic feature than the cathodic reduction of the metal ion constituents. The exact peak potentials for the anodic scans are summarized in Table 3.

Figure 4 gives the anodic differential pulse voltammograms after a preliminary reduction of the minerals

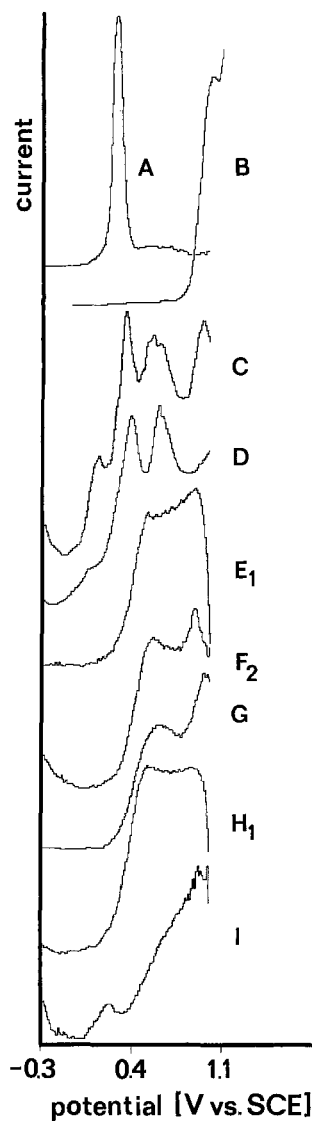


Fig. 3. Abrasive stripping voltammograms (anodic differential pulse mode) of different minerals. See Table 1 for the denotation and Table 3 for the exact values of the peak potentials

Table 2. Peak potentials for the cathodic differential pulse voltammograms (*s* strong signal; *w* weak signal; *sh* shoulder; *b* broad signal; *t* tall signal)

Mineral	E_p [mV vs. SCE]
A	-1665 a, b; -1915 w, t
B	-1195 w; -1515 s; -1740 s
C	-1560 s, b
D	-1455 sh; -1645 s, b
E	-1610 s, b
F	-1600 s, b
G	-1620 s, b
H	-1575 s, b; -1885 w
I	-1255 s, sh; -1625 s, b

to the metals. This technique may be termed "inverse", although some confusion may arise with the usual inverse voltammetry (stripping voltammetry with preliminary deposition from a solution). The obtained voltammograms are of outstanding value for the identification of the minerals, since in many cases the well-known signals of the metals are

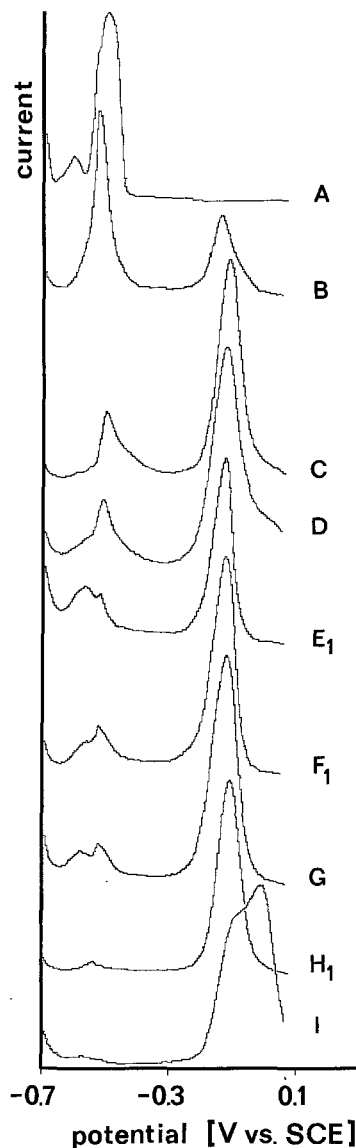


Fig. 4. Abrasive stripping voltammograms (anodic differential pulse mode after preliminary reduction, i.e., inverse mode) of different minerals. See Table 1 for the denotation and Table 4 for the exact values of the peak potentials and peak current ratios

Table 3. Peak potentials for the anodic differential pulse voltammograms (*s* strong signal; *w* weak signal; *sh* shoulder; *b* broad signal; *t* tall signal)

Mineral	E_p [mV vs. SCE]
A	280 s, t
B	1015 sh, t
C	125 sh, w; 350 s, t; 565 s, b; (950)
D	385 s, t; 610 s, t
E	500 s, sh; 870 s
F	525 s, sh
G	615 s, sh
H	515 s and 870 s, strong overlapping
I	230 w

observed. It is interesting to note that the shape of the lead peak depends to some extent on the parent mineral. This can only be understood as a sign that the deposited lead exists in a form predetermined in some way by the structure

of the mineral. Hence the reduction process should be a solid state reaction rather than a reaction proceeding via dissolved ions. The typical structured lead peaks observed in the case of the Pb-Sb-sulfo salt minerals were never observed when Pb-Sb-alloys were studied with abrasive stripping voltammetry [13]. Table 4 gives the peak potentials and peak current ratios for the voltammograms of Fig. 4. Note that there are even certain slight differences for the peak potential of lead. In conclusion it can be stated that the voltammograms (Figs 3 and 4) are sufficient to identify the minerals

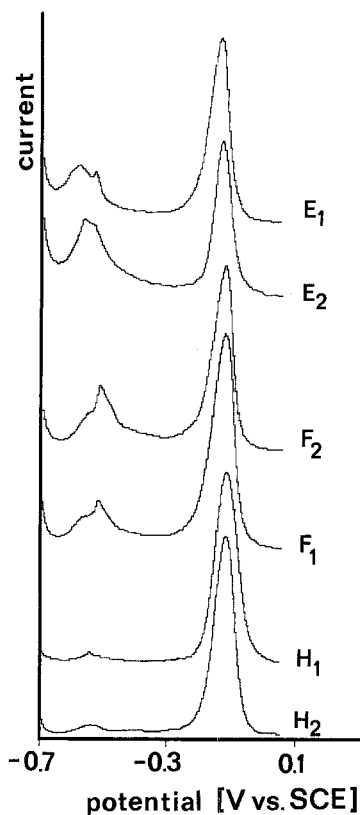


Fig. 5. Abrasive stripping voltammograms (inverse mode) of three different minerals, each of two localities. See Table 1 for the denotation

unambiguously. The high value of the inverse technique is illustrated by Fig. 5 giving the voltammograms of three different minerals, each of two localities. Obviously, the differences arising from the origin are very small and do not hinder the exact identification. Figure 6 shows the inverse voltammograms for two silver containing minerals, andorite and ramdohrite. There is also no problem for their identification. Figure 7 may serve as a useful example for the application of abrasive stripping voltammetry (inverse technique) for the identification of the origin of minerals when their composition strongly depends on their locality. For the mineralogist, grown up with experience in X-ray analysis, it may be surprising that the voltammograms of the fahlores are very different, although their structure is very similar. This is simply due to the fact that voltammograms mirror the chemical composition rather than structure. Finally, Fig. 8 shows the inverse voltammograms of krokoite (PbCrO_4) and cinnabar (HgS). Both voltammograms give evidence for the nature of the metal component.

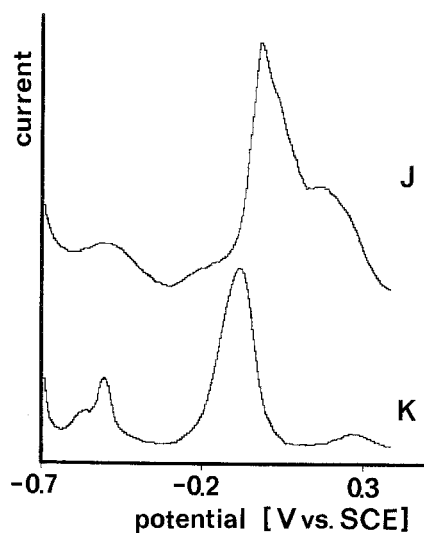


Fig. 6. Abrasive stripping voltammograms (inverse mode) of silver containing minerals andorite (*J*) and ramdohrite (*K*)

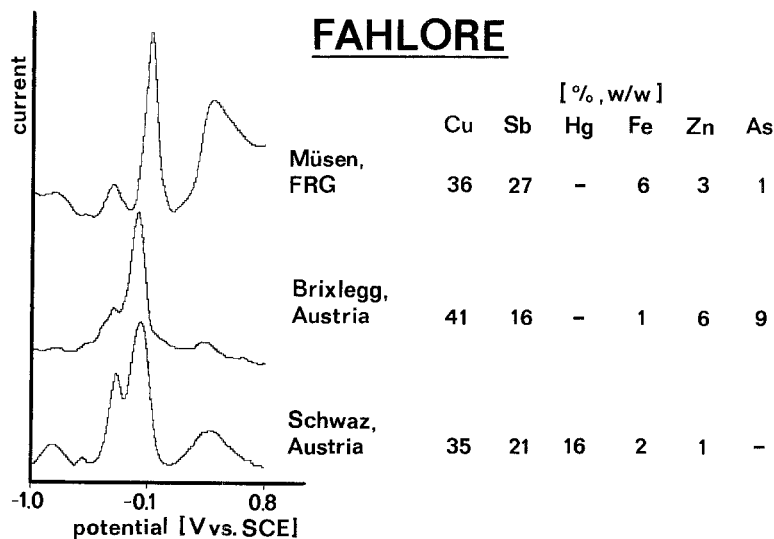


Fig. 7. Abrasive stripping voltammograms (inverse mode) of fahlores from different localities. The electrolyte was 0.1 mol/l $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer

Table 4. Peak potentials for the inverse voltammograms

Mineral	$E_p(\text{Pb})$	$E_p(\text{Sb})$	$i_p(\text{Sb})$	$E_p(\text{Ag})$ [mV vs. SCE]
	[mV vs. SCE]		$i_p(\text{Pb})$	
A	-608/-500	-	-	-
B	-524	-144	0.43	-
C	-504	-124	3.22	-
D	-510	-132	3.99	-
E	-574/-526	-140	3.44	-
F	-554/-524	-132	4.05	-
G	-580/-526	-126	7.07	-
H	-544	-120	19.7	-
I	(-570) ^a	-96/-22	(66.7) ^a	-
J	-490	-10	4.44	+160
K	-568/-518	-82	10.9	+250

^a Due to Pb as an impurity

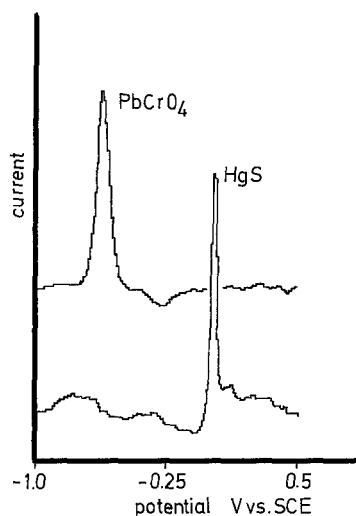


Fig. 8. Abrasive stripping voltammograms (inverse mode) of krokoite (PbCrO_4) and cinnabar (HgS)

Eventually it has to be noted that the described method is applicable to an incountable number of minerals. Since the voltammograms are unambiguous fingerprints not only of the stoichiometric chemical composition but also of structural features of the minerals, the method of abrasive stripping voltammetry can be expected to advance to a method for mineral analysis as valuable as other spectroscopies.

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