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# TERMINOLOGY AND CONVENTION FOR ELECTROCHEMICAL STRIPPING ANALYSIS

(Technical Report)

*Prepared for publication by*

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# Terminology and convention for electrochemical stripping analysis (Technical Report)

## INTRODUCTION

The term electrochemical stripping analysis is applied to a family of procedures involving a preconcentration of the determinand (or a salt or derivative of the determinand) onto the working electrode, prior to its direct or indirect determination by means of an electroanalytical technique [1,2]. Such a combination of an effective accumulation step with an advanced measurement procedure results in a very low detection limit, and makes stripping analysis one of the most important techniques in trace analysis. The original stripping analysis method involved the cathodic electrodeposition of amalgam-forming metals onto a hanging mercury drop (working) electrode, followed by the anodic voltammetric determination of the accumulated metal during a positive-going potential scan [3]. Numerous advances during the 1980s and 1990s, however, have led to the development of alternative preconcentration schemes and advanced measurement procedures that further enhance the scope and power of stripping analysis [4,5]. As a consequence, numerous variants of stripping analysis exist currently, differing in their method of accumulation and measurement. A recent text on stripping analysis is by Brainina & Neyman [6], and recent reviews on adsorptive stripping voltammetry are by Kalvoda & Kopanica [7], van den Berg [8] and Paneli & Voulgaropoulos [9].

Problems in selecting an effective nomenclature for stripping analysis are discussed in this document. Stripping analysis incorporates a two step process—accumulation and determination—and the technique can be considered to be a ‘hyphenated technique’. The method of determination has been included, usually, in naming a particular technique, but often the method of accumulation has not. In some cases, e.g. adsorptive stripping voltammetry, the method of accumulation is given but no indication is given as to whether the determination is cathodic or anodic (or whether it measures a capacitance current due to desorption).

The purpose of this document is to recommend classification, and relevant terminology, for the different procedures used in electrochemical stripping analysis.

### Some existing names of techniques

The term anodic stripping voltammetry (ASV) was used first for the cathodic accumulation of metals as an amalgam followed by their anodic determination [10]. The term cathodic stripping voltammetry (CSV) was used first for the indirect determination of organics as mercury salts, involving anodic oxidation of mercury and subsequently cathodic reduction of the mercury ion [11]. The direct determination of metal ions by cathodic reduction of an adsorbed complex has most often been called cathodic stripping voltammetry [12], but sometimes adsorptive cathodic stripping voltammetry (AdCSV) [13]. The direct determination of adsorbed organics by cathodic reduction has mostly been termed adsorptive stripping voltammetry [14], or cathodic stripping voltammetry [15]. Kalvoda used the term stripping voltammetry with adsorptive accumulation in an early paper which was concerned mainly with adsorption of electroinactive organics followed by their desorptive determination [16]. The term catalytic cathodic stripping voltammetry has been applied to methods involving the coupling of the reduction of a metal ion in an adsorbed metal complex with its chemical regeneration by a chemical oxidant in the solution [17].

The term adsorptive transfer stripping voltammetry (AdTSV) has been applied to cases, particularly those involving studies of large biomolecules, in which the electrode is transferred to a different electrolyte after accumulation and before determination [18]. Abrasive stripping voltammetry (AbSV) has been used to describe the technique in which solid sample containing the chemical species of interest is transferred to the electrode mechanically [19]. Bond (personal communication) has pointed out that the term abrasive stripping voltammetry is often used in rather unsatisfactory ways, e.g. when there is no stripping or even no analytical application, and has asked that some comments be made by the present authors: these follow. This abrasive transfer technique has been used for qualitative analysis and also for

major component determination based on the ratio of measurements of all (usually two) components, but has been extended very advantageously to fundamental electrochemical studies of the transferred finely divided solid. As it is not a trace quantitative analysis technique for the determination of chemical species in solution samples (the solid sample arrives on the electrode without going through a solution phase), the technique is only related superficially to the other techniques described here. The use of a term such as abrasive transfer voltammetry might be more appropriate for this technique, particularly when it is used for fundamental electrochemical studies. It is not discussed further here.

Johnson & Allen [20] developed a technique which they termed stripping voltammetry with collection (SVWC) which utilises a rotating ring-disc electrode. Accumulation and stripping of a metal or insoluble metal salt is carried out on the disc electrode, as is usual in ASV, but a reproducible proportion of the metal ion that is stripped subsequently from the disc electrode is collected at the ring electrode which is set at a suitable fixed potential. Because the ring electrode is at a fixed potential the background current associated with it is almost constant and can be compensated for. This allows lower detection limits to be reached than with conventional ASV for which the background current changes during the scan.

The term potentiometric stripping analysis (PSA) has been used for the technique concerned mainly with the determination of metals accumulated on a mercury electrode by monitoring the change of potential with time which occurs during chemical oxidation of the accumulated metal [21], although some workers routinely use other electrodes such as gold [22]. PSA can be carried out also using chemical reductants [23], and also, electrochemically, using an applied constant current [24]. Zie & Huber [25] have described a technique which they term constant current enhanced potentiometric stripping analysis (CCEPSA), in which a constant current is imposed on the electrode during the stripping step. By this means some of the metal stripped is redeposited during the stripping period, thus extending the potentiometric stripping time and enhancing the sensitivity of the method. An analogous technique had been used previously in stripping voltammetry [26]: in this case part of the metal stripped voltammetrically is redeposited during the stripping by a chemical reductant. These two latter techniques [25,26] are forms of catalytic stripping analysis.

## DISCUSSION

### The term 'stripping'

The term 'stripping' used in naming the original technique, anodic stripping voltammetry, describes exactly the process that is occurring during the voltammetric scan. After cathodic accumulation of metal ion in the mercury surface as its amalgam, the metal is stripped from the mercury anodically to form its ions back in solution. The term is not so strictly applicable, however, in describing some other electrochemical stripping methods. The products of reduction of many adsorbed organic compounds, for example, remain adsorbed on the electrode, and are not stripped from the electrode. When the metal in an adsorbed metal complex is reduced, the complexing agent might be stripped from the electrode, but the metal is often converted to its amalgam. Nevertheless, in all cases, all of the electroactive species present on the electrode is changed and therefore the term 'stripping' can be considered to be a close approximation to what in effect occurs.

### The diversity of stripping analysis techniques available

Previously an attempt was made to list, as comprehensively as possible, and in general terms, the types of method used for accumulation and determination in stripping voltammetry [27]. A preliminary discussion of the nomenclature of stripping voltammetry was also published [28]. These papers did not consider the technique which has been termed potentiometric stripping analysis (PSA), but this technique is included here.

Methods of voltammetric determination are normally either cathodic or anodic owing to the nature of the technique, although tensammetric determination, in which capacitance currents, observed during a desorption process, are monitored [16], can also be considered here usefully, particularly as desorption is the opposite process to adsorption. Accumulation can be cathodic, anodic or adsorptive (or a combination of either cathodic or anodic with adsorptive accumulation): anodic and cathodic accumulation methods extend far beyond the well known accumulation of mercury salts of the determinand, and of metal

amalgam. If chemically modified electrodes are used accumulation can also involve ion-exchange, partition, complexation, and affinity processes [29,30].

In considering a general nomenclature some more recent and less well known methods of accumulation should be considered [27]. Some chemical species are determined, in the presence of copper(II), as copper(I) complexes or salts [31]. Determinands can be accumulated in a reduced form, and can then be determined by further reduction [32].

Some determinands are reduced reversibly and their reduction products are also adsorbed on the HMDE. Because of this they can be determined by adsorption and reduction in the normal way, or they can be accumulated cathodically and then determined by reoxidation anodically [33,34].

Selenium(IV) can be accumulated as  $Cu_2Se$ , in which both selenium(IV) and copper(II) are reduced [35]. Some stripping methods, such as particular methods for tin(IV) [36] and arsenic [37], involve an intermediate electrochemical step, and others involve a change of electrolyte solution after accumulation [18]. The coupling of the reduction of a metal ion in an adsorbed metal complex with its chemical regeneration by a chemical oxidant in the solution gives rise to higher (catalytic) currents and lower detection limits [17].

The technique which has been termed PSA has been used mainly for the determination of metal ions, in which accumulation is effected cathodically by forming the metal amalgam, followed by potentiometric determination of the metal by monitoring the electrode potential as the metal is oxidised by a chemical oxidant [21]. Adsorptive accumulation of determinands can be used with PSA: Wang *et al.* [38] have determined trace amounts of RNA by PSA at a carbon paste electrode after adsorptive accumulation. Stripping can also be carried out using chemical reductants [23] and using an applied constant current [24].

The question arises as to whether it is possible to produce a system of nomenclature for stripping analysis methods, which would cover satisfactorily, not only the more straightforward methods, but also those above which include more unusual features.

### **Towards a comprehensive acronym notation**

One possible system of indicating the chemical and electrochemical processes involved in individual stripping voltammetric methods, including those described above, as acronyms, was suggested by Fogg [28]. This system can be extended readily to include PSA. Consideration of this system gives an indication of the difficulty of producing a simple acronym system to describe the complexity of some stripping analysis methods. For reasons of clarity at this stage, and to allow time for further consideration before making recommendations, the details of this system are not discussed here.

### **The case for a simple nomenclature**

There may be a case for expressing the chemistry in any new unusual method of stripping analysis in a form such as that outlined by Fogg [28]. This would certainly highlight the fact that the chemistry involved is more complicated than may at first appear. Clearly, however, a simpler nomenclature is required for general use.

The acronyms ASV and CSV have been accepted widely for anodic and cathodic stripping voltammetry. AdSV is used by several authors for adsorptive stripping voltammetry, although this has tended to be restricted to the adsorption and reductive (or desorptive) determination of organic molecules. The adsorption and reduction of metal complexes to determine the metal ion has more usually been termed cathodic stripping voltammetry, or, less often, adsorptive cathodic stripping voltammetry (AdCSV). There appears to be a case for discontinuing the use of AdSV and AdCSV, and simply using the term CSV [or stripping tensammetry (ST) (see below) when there is adsorptive accumulation and desorptive determination] for these examples.

In describing some methods the use of the terms ASV and CSV can be unhelpful, as no indication is given about the more complicated nature of any intermediate step or the accumulation step. In some cases where the use of CSV or ASV might unintentionally mislead a reader, there is a case for using the simpler term stripping voltammetry (SV) as a means of flagging the fact that the method is more complicated than

the use of CSV or ASV would imply. This would cause the reader to look more closely at the nature of the method involved.

An increased use of the term stripping voltammetry to replace terms such as cathodic stripping voltammetry, anodic stripping voltammetry and adsorptive stripping voltammetry is recommended below. [Van Leeuwen (personal communication) has pointed out that the term cathodic voltammetry is not used to describe a particular technique. The term voltammetry is used simply. By analogy there is no requirement to use terms such as cathodic stripping voltammetry instead of stripping voltammetry.]

### Stripping tensammetry

Electroinactive organic compounds that adsorb on the electrode have been determined by monitoring the capacitance current observed when they are desorbed during a potential scan [16]. This method has been termed adsorptive stripping voltammetry in the literature, no distinction being made in the name of the technique between methods in which the adsorbed molecule is simply desorbed (i.e. without reduction) and those in which the adsorbed molecule is reduced.

The suggestion here is that the nonfaradaic method should be termed stripping tensammetry (ST). The term tensammetry, which indicates the measurement of a current produced by a change of surface tension at the electrode surface, has been used extensively for the nonfaradaic form of polarography [39].

### Chemically modified electrodes

Chemically modified electrodes can be used to accumulate determinands using ion-exchange, partition, complexation or affinity processes [29,30]. The form of complexation accumulation referred to here differs from that discussed above, as in chemically modified electrodes the ligand is an integral part of the electrode, often being covalently bonded to some component of the chemically modified electrode rather than being present in the solution. An IUPAC document entitled 'Analytical aspects of chemically modified electrodes: classification, critical evaluation and recommendation' [40].

### PSA, stripping potentiometry, or stripping chronopotentiometry?

The diversity of possible techniques is more pronounced for stripping voltammetry, but it is clear that any system of nomenclature for electrochemical stripping analysis must be equally satisfactory for the technique which has been termed PSA as for stripping voltammetry. PSA has been used mainly for the determination of trace amounts of metals. The metal ion is accumulated cathodically as in ASV to give its amalgam, but then is stripped from the electrode by means of a chemical oxidant at a fixed concentration. Determination is made by monitoring the change of electrode potential with time during the stripping process: the transition time is related to determinand concentration. Therefore the determination method is chronopotentiometry rather than potentiometry.

For this reason the term stripping chronopotentiometry (SCP) is recommended rather than either PSA or stripping potentiometry.

### NOTATION AND TERMINOLOGY

The following terms are recommended for use in electrochemical stripping analysis:

- (i) Electrochemical stripping methods are methods involving the preconcentration of a determinand onto the working or indicator electrode, before it is determined electrochemically.
- (ii) Stripping voltammetry (SV) involves the determination of an accumulated determinand by monitoring the faradaic current during a potential scan.
- (iii) Stripping tensammetry (ST) involves the determination of an accumulated determinand by monitoring the capacitance current produced by a desorption process during a potential scan.
- (iv) Stripping chronopotentiometry (SCP) involves the determination of an accumulated determinand by observing the change of electrode potential with time during the stripping (at a constant rate) of the accumulated determinand either chemically or electrochemically. The transition time, i.e. the time

between two significant changes in electrode potential, is related to determinand concentration. [Jagner (personal communication) has indicated that, when carrying out stripping using a constant current, chemical stripping can be eliminated completely only by using unacceptably short transition times.]

The terms above are preferred but the following terms are recognised as secondary terms because of their widespread use:

- (i) Cathodic stripping voltammetry (CSV) involves the electrochemical reductive determination of a determinand by stripping voltammetry. It is recommended that this term be used only in cases where it describes the chemistry involved in the particular method unambiguously, i.e. in methods in which the determinand is accumulated either anodically (e.g. as a mercury salt) or by direct adsorption (without reduction or oxidation) (in the case of an organic compound), and is then determined cathodically. The term stripping voltammetry should be used where the overall process is more complicated to flag that the chemistry is more detailed, and in order not to mislead.
- (ii) Anodic stripping voltammetry (ASV) involves the electrochemical oxidative determination of a determinand by stripping voltammetry. It is recommended that this term be used only in cases where the term describes the chemistry involved in the particular method unambiguously, i.e. in methods in which the determinand is accumulated either cathodically (in the case of a metal ion) or by direct adsorption (without reduction or oxidation) (in the case of an organic compound), and is then determined anodically. The term stripping voltammetry should be used where the overall process is more complicated to flag that the chemistry is more detailed, and in order not to mislead.
- (iii) Adsorptive stripping voltammetry (AdSV) is applied to stripping voltammetric techniques in which accumulation is effected by adsorption of (mainly) organic determinands. The use of the term can be justified less in the case of the adsorption of metal complexes in determining metal ions, although Kalvoda (personal communication) has pointed out that metal complexes adsorb by virtue of adsorption by their ligands. The term should not be applied when there is a change of oxidation state of the metal ion during the accumulation (e.g. in the accumulation of copper(I) complexes or salts) or in other cases where an organic compound is being accumulated, and determined indirectly, as a metal salt or complex (e.g. as mercury salts or nickel complexes).
- (iv) Potentiometric stripping analysis (PSA) and stripping potentiometry (SP) are general terms synonymous with stripping chronopotentiometry.

Various waveforms have been used in the stripping step of stripping voltammetry. These can be indicated as prefixes to the primary and secondary voltammetric terms used above. Examples are linear sweep stripping voltammetry (LSSV), differential pulse cathodic stripping voltammetry (DPCSV) and square wave adsorptive stripping voltammetry (SWAdSV).

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