

## Chemical amplification—A novel approach to ultratrace analysis

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**Abstract.** The lowest concentration that can be estimated with 100% error in chemical analysis by instrumental technique is referred to as detection limit. It is equal to the ratio of twice the background signal to the magnitude of analytical signal corresponding to a concentration of unity. Detection limit (DL) could be improved if the analytical signal alone could be selectively amplified without affecting the background. It is shown that this could be achieved by chemical amplification. Atomic amplification of two or three orders of magnitude could be obtained by combining two chemical amplifications in series. It is demonstrated that by using heteropoly acid formation as the first amplification reaction and determining molybdenum in the heteropoly acid by catalytic DC polarographic wave, a detection limit for the hetero atom of less than a ppb can be obtained. It is pointed out that the approach of selectively amplifying analytical signals by tandem chemical amplification reactions makes it possible to perform ultratrace analysis (ppb level) with classical instrumental analytical techniques which have DL at ppm level.

**Keywords.** Chemical amplification; trace analysis; ultratrace analysis; DC polarography; signal-to-background ratio.

### 1. Introduction

Chemical characterisation by instrumental methods is based on the proportionality between the analytical signal given by a particular species and its concentration. Experimentally it is not possible to measure analytical signal ( $S$ ) alone. Only the total signal ( $S_T$ ) which is the sum of analytical signal and background ( $B$ ) can be measured. Consequently, one uses in practice  $S_T$  instead of  $S$ , which amounts to assuming a proportionality between  $S_T$  and analyte concentration. This introduces an error in the estimation, which increases with the ratio of background-to-signal. The use of  $S_T$  instead of  $S$  also sets a limit to the lowest detectable concentration. It is customary to define this background limited detection limit (BLDL) as the concentration at which the signal-to-background ratio (SBR) is unity. Incidentally it may be pointed out that this will correspond to a concentration at which the measurement error is 100%. Practically all measurements yield only the total signal and therefore detection limits of almost all the instrumental methods of chemical analysis are set by background. For the sake of brevity we shall refer to BLDL as detection limit (DL).

Another way of defining DL is signal,  $S_T$ , is twice that given by the system free from the species that is analysed (*i.e.*  $S_T = 2B$  since  $S = B$ ). In the light of this definition, it is possible to relate the slope of the calibration curve ( $m$ ), which is equal to the magnitude of analytical signal when the concentration is unity, to the detection limit. It is readily seen that  $S/B$  will be unity at a concentration of  $2B/m$ , which is nothing but the reciprocal of half of the SBR at a concentration of one unit. In other words, if a species can be estimated by different methods then the method that gives the largest SBR at a concentration of one unit will give the lowest DL.

From the expression  $DL = 2B/m$ , it is obvious that DL can improved by the

suppression of background (*i.e.* decreasing  $B$ ) or by enhancing the analytical sensitivity (*i.e.* by increasing  $m$ ) or by both. Whichever is the procedure employed, the result is an improvement in SBR and a consequent lowering of DL since it is inversely proportional to SBR at unit concentration.

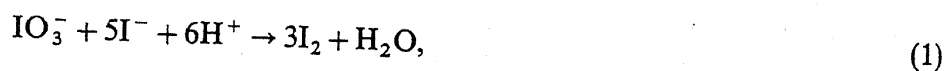
The need to estimate species at ppm and ppb levels and the necessity to analyse small quantities of samples demand analytical techniques that have DL at sub ppb level. We have been looking into the possibility of improving the detection limit of classical instrumental analytical techniques through improvement of SBR and this communication summarises some of our results.

The background arises from factors like random noise, drift and those that are unique to the particular technique. Of these the last mentioned factor contributes most to the background; in the spectrophotometric method this factor stems from stray light, scattering, reflection etc., in the electrochemical methods current required to charge the interfacial capacitance is the major cause of background and so on. Unlike random noise, the elimination of the background characteristic of the technique is not easy. Improvement of SBR by the suppression of background will be discussed elsewhere.

Selective amplification of analytical signal alone without increasing background can be effective in improving detection limit since it increases the analytical sensitivity. Electronic amplification cannot achieve this since it is not selective. Such an amplification can be realised by chemical amplification. We will discuss here the use of this technique for improving DL.

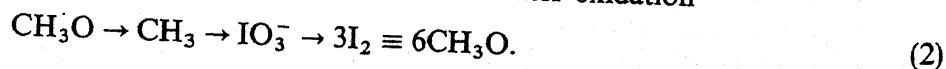
## 2. Chemical amplification

Leipert (1929) was the first to suggest a chemical amplification method to estimate low concentrations of iodide. In this method iodide is oxidised to iodate by bromine water; after excess bromine is destroyed, iodide is added in excess to bring about the following reaction



and the liberated iodine is titrated with sodium thiosulphate. It is seen that each equivalent weight of iodide present in the original solution will consume six equivalents of thiosulphate *i.e.* the original equivalence has been amplified by a factor of six. This class of chemical reaction where the component to be analysed itself is amplified and measured is called direct chemical amplification.

Vieböck and coworkers (Vieböck and Brecher 1930; Vieböck and Schwappach 1930) proposed a method of estimation of alkoxy group using the so-called Leipert reaction described above. In this method, the alkoxy group is converted into alkyl iodide which is decomposed and the iodide is estimated after oxidation



Here again an amplification factor of 6 for the alkoxy group is obtained. This class of reaction where the constituent required is not amplified and measured but a species associated with it, may be called indirect chemical amplification reaction.

Besides these types of reactions, reactions catalysed by homogeneous catalysts and cycling reactions can also yield chemical amplification.

These chemical amplification reactions have been mostly used in the past for

improving the sensitivity of volumetric and gravimetric methods and has been reviewed by Belcher (1968) and Blaedel and Boguslaski (1978). Excepting for a few studies describing the use of indirect amplification reactions for accomplishing indirect estimation of constituents by atomic absorption spectrometry (*e.g.* Kirkbright *et al* 1967; Ramakrishna *et al* 1969) utility of chemical amplification reaction in instrumental analysis has not been explored. There is practically no study on the use of these reactions for improving the detection limits of instrumental analytical methods. We present in this paper some of our results on the feasibility of improving by several orders the detection limit of analytical techniques, by employing chemical amplification to enhance SBR.

### 3. Enhancement of analytical sensitivity by single chemical amplification reaction

Direct chemical amplification reactions are rare. Many of the indirect chemical amplifications quoted in the literature are specific. Only those based on precipitation of metals with 8-hydroxyquinoline and determination of the precipitate by titration with bromide-bromate appear general enough for the application of chemical amplification method to the determination of metals (Berg 1926). But this reaction is not well suited for instrumental methods.

Extraction of ion associates with a suitable organic reagent and determination of the co-ion either in the organic phase or after back extraction can be used as a general method of chemical amplification. We have examined the use of this principle to estimate boron by charging current compensated DC polarography (Kannan *et al* 1982). In this method, the ion-pair formed from the anionic complex of boron with mandelic acid and the cationic complex of tris 1, 10 phenanthroline cadmium (II) is selectively extracted with MIBK, cadmium from the organic phase is stripped into 1 M HCl and determined polarographically after destroying phenanthroline. In terms of weight the amplification factor is 5. A typical polarogram for 55 ppb boron equivalent of cadmium is shown in figure 1 to illustrate the ultratrace analytical capability. This approach, besides increasing the analytical sensitivity also helps to provide a favourable analytical signal. In the example cited above, boron being electro-inactive does not yield a signal for its electrochemical determination but this method helps us to measure boron by the electrochemically favourable signal of cadmium.

An allied class of reactions that can be considered for the chemical amplification is

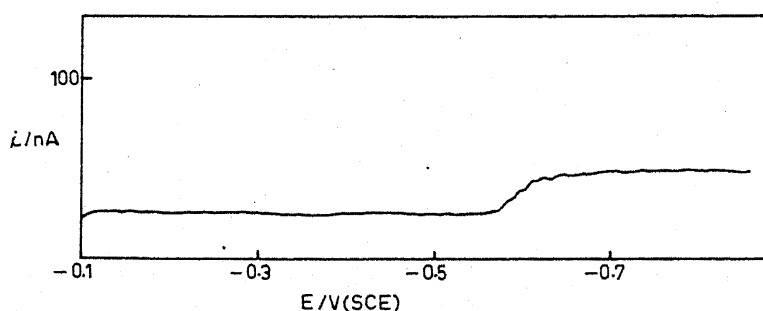
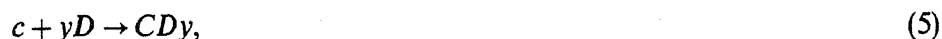


Figure 1. Charging current compensated DC polarogram of cadmium equivalent to 55 ppb of boron.

the formation of ternary complexes. Both these approaches give amplification factors that are less than 10. A particularly fascinating method is to use heteropoly acids for chemical amplification, which gives an atomic amplification of 12. This will be dealt with in the next section.

### 3.1 Series coupling of chemical amplification reactions

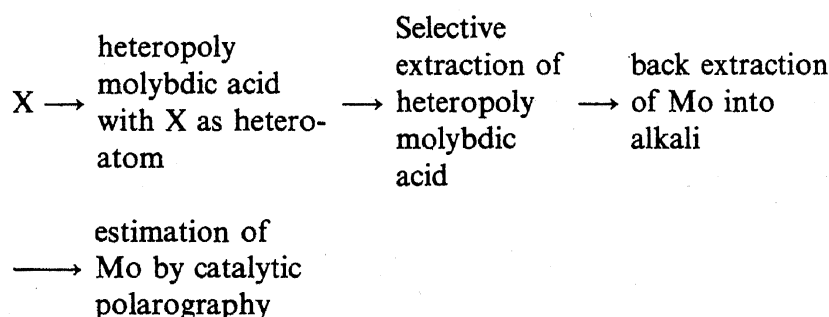
Consider the following scheme for the estimation of  $A$



Estimation of  $A$  is accomplished by isolating  $AC_x$ , decomposing it to liberate  $C$ , which is converted into  $CD_y$ , separating  $CD_y$ , and estimating  $D$  in  $CD_y$ . It is seen that the scheme combines serially two chemical amplification steps *viz* liberation of  $x$  atoms of  $C$  for every atom of  $A$  and generation of  $y$  atoms of  $D$  for each atom of  $C$ . The atomic amplification factor for the first amplification step is  $x$  while that for the second step is  $y$ . It is readily seen that each atom of  $A$  yields  $x \cdot y$  atoms of  $D$ . In other words the total amplification factor for series coupling of chemical amplification reactions is equal to the product of the atomic amplification factors of each step. Thus it is possible to achieve much larger amplification factors using chemical amplification reactions in tandem than what can be got by a single amplification.

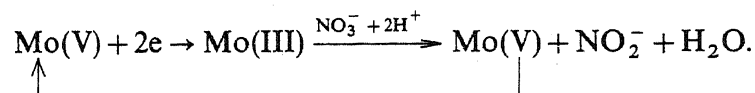
A simple way of realising the above scheme in practice, is through cycling as was done by Geilmann and Bartlingck (1942) to estimate traces of iodine. They oxidised iodine to iodate, liberated iodine by Leipert reaction, extracted it into  $CCl_4$ , back-extracted iodine into  $NaHSO_3$  solution, oxidised the resulting iodide to iodate and estimated the iodine liberated from iodate. In this process the Leipert reaction has been used twice in succession resulting in an overall amplification of 36. This relatively simple approach suffers from the drawback of difficulties in isolation.

We found that this problem could be solved by involving the species generated by the first amplification reaction in another type of amplification reaction. As an example let us consider the following scheme



In the first step  $12(MoO_4)^{2-}$  are released for each hetero atom X yielding an amplification factor of 12. Instead of directly estimating Mo resulting from the first amplification reaction, it is estimated by a cycling type of amplification reaction. In this, the  $Mo(VI)$  is reduced at the dropping mercury electrode in the presence of an oxidising

anion like  $\text{NO}_3^-$ . The wave due to the 2-electron reduction of Mo(V) to Mo(III), known as the catalytic wave, exhibits a very much larger height than the diffusion controlled wave, because of the cyclic generation and reduction of the electroactive species, Mo(V), in the following manner,



The amplification factor for the second step is dependent on temperature and can vary from 20 to 50 for the temperature range of 20 to 50°C. The total amplification (atomic) achieved by coupling heteropoly acid formation with the estimation of Mo by catalytic DC polarography is from 240 to 600 depending on the temperature. The ultratrace analytical capability of DC polarography employing the above type of chemical amplifications in tandem is seen from the DC polarogram of Mo equivalent to 2.2 ppb of P (Kannan *et al* 1983).

The advantages of this approach as revealed by our work are: (i) analytical sensitivity is enhanced by more than two orders of magnitude resulting a detection limit of better than 0.5 ppb, 0.25 ppb, 0.5 ppb (Kannan *et al* 1980) and 0.9 ppb (Kannan *et al* 1983) respectively for silicon, phosphorous, arsenic and boron. (ii) The scheme is applicable to a number of elements since at least 35 elements are known to be capable of functioning as the heteroatom. (iii) The method is capable of further extension by taking advantage of the fact that the peripheral atoms may be substituted to yield 1:11 compound. (iv) The amplification factor can be calculated. Neither does it vary from system to system nor with the concentration. Therefore in this method the concentration can be calculated from theory and one does not have to rely on calibration curve. This makes the method very reliable. (v) Specificity is ensured from the heteropoly acid formation and selective extraction of the same. (vi) The background is practically unaffected and hence the method yields an improvement in SBR by more than 2 orders of magnitude.

#### 4. Conclusions

Chemical amplification reactions can be employed as a method of selectively

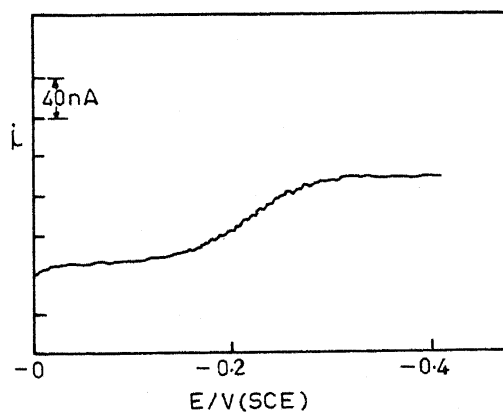


Figure 2. Charging current compensated catalytic DC polarogram of Mo equivalent to 2.2 ppb of phosphorous.

amplifying the signal without increasing the background. Combining chemical amplifications in series gives an atomic amplification of more than two orders of magnitude and the corresponding weight amplification is more than three orders of magnitude. Though the utility of the principle of sequential chemical amplification reactions for improving DL has been illustrated here by using DC polarography, it is applicable to any analytical technique. By employing this approach it is possible to convert classical instrumental analytical technique with DL of about a ppm into ultratrace analytical techniques that exhibit ppb analytical capability.

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