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COMMISSION ON ANALYTICAL REACTIONS AND REAGENTS*

**RECOMMENDATIONS ON USE OF THE
TERM AMPLIFICATION REACTIONS**

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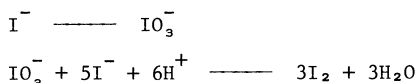
Abstract - The first amplification reaction was probably introduced by Friedrich Mohr in 1853, in which iodide is oxidised to iodate; iodide and acid are then added in excess and six times the original amount of iodine is released. Several amplification methods are based on this process, but the lack of an acceptable definition has led to the indiscriminate use of the term in the literature. Stated simply, an amplification reaction is one which replaces the conventional reaction used in a particular determination so that a more favourable measurement can be made. The reaction sequence can be repeated to provide further increase in measurement. The new definition embraces both direct and indirect amplification, but excludes those processes which do not involve magnification of the constituent being determined, or of an associated constituent. Such reactions are now termed enhancement reactions. Appropriate examples are given.

A certain looseness in the use of the term "amplification" is to be found in the literature. To avoid further uncertainty, amplification reactions are now defined as follows:

An amplification reaction is one which replaces the conventional reaction used in a particular determination so that a more favourable measurement can be made. The sequence can be repeated to provide a further favourable increase in measurement.

Sometimes the term multiplication is used synonymously with amplification (Note 1), but this usage is not recommended; hence the term multiplication should be avoided.

The first amplification method was probably introduced by Friedrich Mohr in 1853 (1). He determined iodide by oxidation to iodate with chlorine water. After the excess of chlorine was removed by evaporation, excess of iodide was added and six times the original amount of iodine was liberated.



The reaction was studied by Winkler (2) (1900) who also used chlorine water. Hunter (3) (1909) used hypochlorite as the oxidant. Bromine water, the most convenient oxidant, appears to have been used first by Bugarszky and Horvath (4) (1909).

These methods attracted little attention until 1929 when Leipert (5) described a new titrimetric method for the determination of iodine in organic compounds on the micro-scale. Before this time it had not been possible to determine iodine satisfactorily by titrimetric methods on the micro-scale, because of the unfavourable equivalent weight of iodine. For example, in the conventional method for the determination of iodide by oxidation to iodine,

$$1 \text{ ml } 0.01\text{M Na}_2\text{S}_2\text{O}_3 \equiv \frac{1}{2} \times 0.01 \times 2 \times 126.9 \text{ mg I}_2 = 1.269 \text{ mg I}_2$$

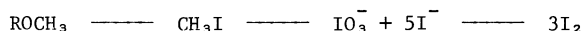
But by the amplification method,

$$1 \text{ ml } 0.01\text{M Na}_2\text{S}_2\text{O}_3 \equiv \frac{1.2690}{6} \text{ mg} = 0.2115 \text{ mg I}_2$$

This particular amplification process is often referred to incorrectly as the Leipert method, but this description only applies to the method for the determination of iodine in organic compounds. It is recommended that the process in which iodide is oxidised to iodate to

achieve a more favourable measurement be termed the Mohr amplification process (Note 2).

Vieböck and his co-workers (6) later described a method in which the same principle was used for the indirect determination of alkoxy, by oxidation of the iodide liberated from the distilled alkyl iodide.



There are two types of amplification:

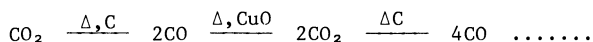
- (a) Direct Amplification where the constituent to be determined is amplified directly and it is this constituent which is finally measured.
- (b) Indirect Amplification where the constituent required is associated with some other constituent which is then amplified and measured (7).

The Leipert method is an example of the use of Direct Amplification and the Vieböck method of the use of Indirect Amplification.

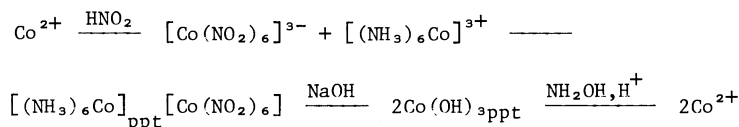
TYPICAL EXAMPLES OF AMPLIFICATION (Note 3)

Direct Amplification

1) Carbon dioxide (8)



2) Cobalt (9)



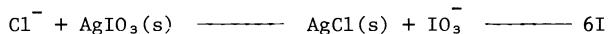
(In this method, the Co^{2+} is determined by titration with EDTA)

3) Sodium (Use of Ion-exchange Resins) (10)

Sodium can be amplified by passage through a column containing resin in H^+ -form. The released H^+ is led into a column containing resin in the Na^+ -form. The released Na^+ is collected. The original H^+ -form resin is now treated with H^+ to release the Na^+ retained during the first exchange reaction. This Na^+ is added to that already collected and the solution is evaporated to give twice the amount of sodium originally present. The cycle can then be repeated.

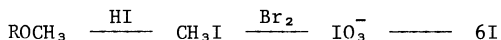
Indirect Amplification

1) Chloride (7)



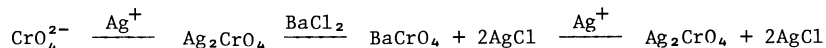
(The metathesis can take place with mercury(I) and mercury(II) iodates equally well.)

2) Alkoxy Groups, e.g. Methoxy (6)

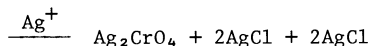
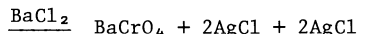


3) Amplification of Metal Ions (10)

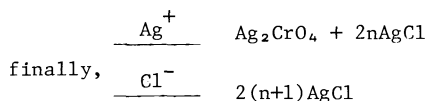
Chromate (or silver by direct amplification)



The process is then repeated; on each treatment with barium chloride, an amount of silver chloride twice the original chromate is produced:



After n-times, there is 2n moles of AgCl for one mole of CrO_4^{2-} originally present:



This sequence of reactions can also be used to amplify phosphate, by precipitation of silver phosphate and its conversion to silver chromate.

There are many reactions which enable a favourable measurement to be made in which the constituent which is finally measured has not been magnified in any way. An example of this type is when phosphorus is determined by formation of 12-molybdophosphoric acid and determination of the molybdenum gravimetrically, titrimetrically, spectrophotometrically, or by atomic absorption spectrometry. The enhanced measurement in this case is achieved because of the very favourable Mo/P ratio of 12:1. Such reactions are often referred to as amplification reactions, but it is not recommended that this type of reaction be so named. Instead it is recommended that these reactions be termed enhancement reactions.

NOTES

1. It has not been possible to establish when the term "amplification" was first used, nor by whom. Emich (11) used the terms "multiplication" and "magnification" in a descriptive sense.
2. It is true that Mohr used chlorine water and Leipert the more convenient bromine water. But this is only a modification of Mohr's original process. In any case Bugarszky and Horvath (4) used bromine water twenty years before Leipert.
3. No attempt is made here to provide a complete classified list of amplification reactions. For further information on this subject, the available reviews should be consulted (see Refs. 12 and 13).

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