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CLASSIFICATION AND USE OF TERMS FOR AMPLIFICATION AND RELATED REACTIONS

(IUPAC Recommendations 1999)

Prepared for publication by
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Classification and use of terms for amplification and related reactions (IUPAC Recommendations 1999)

Abstract: A systematic classification scheme is given for the various types of amplification and related reactions currently available. The report extends and refines earlier IUPAC recommendations [*Pure Appl. Chem.* **54**, 2553–2556 (1982)] to include non-multiplication reactions.

INTRODUCTION

Following recent reviews [1,2] of amplification and related reactions it is appropriate to refine the earlier IUPAC recommendations [3] on the use of the term 'amplification reactions' to include non-multiplication reactions. The earlier report dealt solely with direct and indirect amplification (multiplication) reactions.

Amplification reactions can be classified using terms defined below according to the scheme presented in Fig. 1.

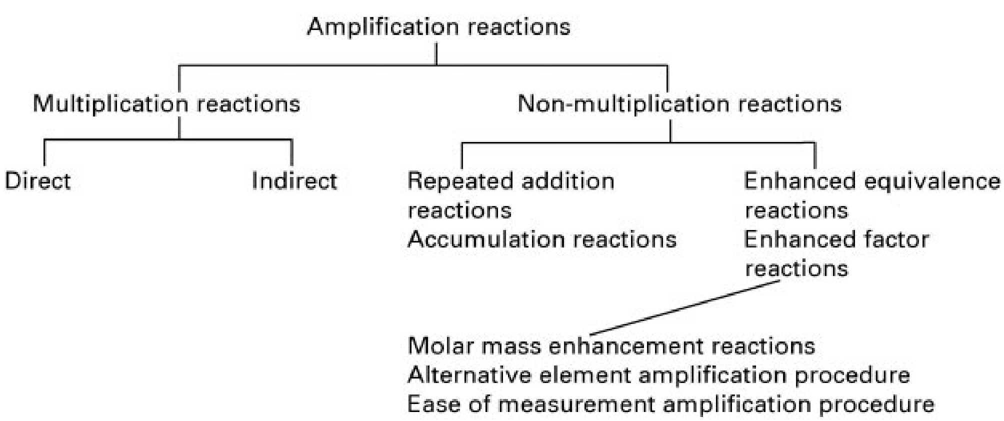


Fig. 1 Classification of the various types of amplification reaction.

The scheme outlined distinguishes between multiplication reactions, which involve reaction cycles in which a species is multiplied to an integral number of the same species in each cycle prior to measurement, and non-multiplication reactions where this is not so. In addition the scheme deals with the confusion that may arise in that the mathematical process of repeated addition, as occurs in another type of amplification, is called multiplication. Finally, it recognises that amplification has been used to describe a perceived facilitation of measurement by changing the basis of measurement or by enhancing sensitivity by increasing the amount of material (not necessarily the starting material) available for measurement.

The following terms are recommended:

Multiplication reactions

Direct multiplication reaction

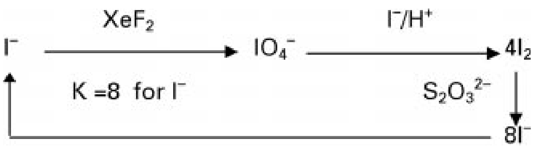
This is a reaction sequence in which the species to be determined is converted by a cycle of chemical reactions into a multiplied number of the same species prior to measurement. The amplification factor after repeating the cycle n times is K^n where K is the amplification factor for a single cycle. For example, the oxidation of iodide by xenon difluoride [4] to periodate followed by reaction with added iodide in acidic solution to form iodine and thence reduction of the iodine back to iodide (8 ions per original iodide ion present) with thiosulphate can be repeated:

$$I^- + 4XeF_2 + 4H_2O \rightarrow IO_4^- + 4Xe + 8HF$$

$$IO_4^- + 7I^- + 8H^+ \rightarrow 4I_2 + 4H_2O$$

$$4I_2 + 8S_2O_3^{2-} \rightarrow 8I^- + 4S_4O_6^{2-}$$

This can be represented as a cycle, with amplification factor 8 (Scheme 1).



Scheme 1

Indirect multiplication reaction

This is a reaction sequence in which the species to be determined is first stoichiometrically converted to or associated with a species which can take part in a direct multiplication reaction sequence.

The classical example of this is Vieböck's method [5,6] for the determination of methoxyl groups. The methoxyl compound is reacted with hydriodic acid to form methyl iodide, which is distilled out and collected in bromine water which displaces the iodine and then oxidises it to iodate. The iodate is treated with iodide from an external source to form iodine, which can then be reduced back to iodide (6 ions per methoxyl group originally present). The reaction sequence from iodide to iodide can be repeated and is an indirect multiplication of the methoxyl group following initial formation of methyl iodide:

$$CH_3OR + H^+ I^- \rightarrow CH_3I + ROH$$

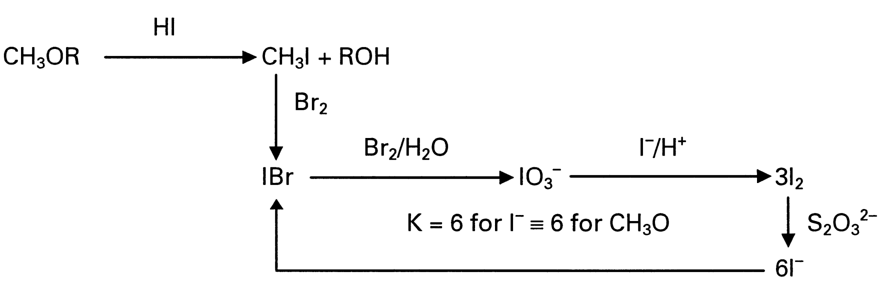
$$CH_3I + Br_2 \rightarrow CH_3Br + IBr$$

$$IBr\ (\text{i.e. } I^+) + 2Br_2 + 3H_2O \rightarrow IO_3^- + 6H^+ + 5Br^-$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$3I_2 + 6S_2O_3^{2-} \rightarrow 6I^- + 3S_4O_6^{2-}$$

which can be shown as a cycle with an amplification factor of 6 (Scheme 2).



Scheme 2

Good accuracy in both direct and indirect amplification depends critically on the extent of complete separation or destruction of the reagent used for the initial oxidation state change in the reaction sequences.

Non-multiplication reactions

Repeated addition reaction or accumulation reaction

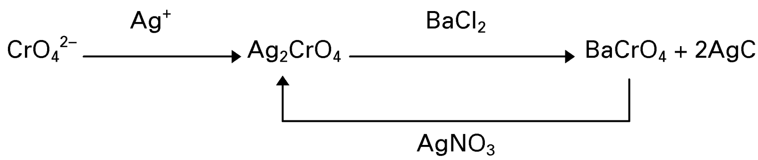
This is a cycle which adds a constant amount of product each time the cycle is repeated. For example, after chromate has been precipitated from neutral solution with silver ions the silver chromate can be reacted with barium chloride solution to form the less soluble silver chloride and barium chromate. The barium chromate can be converted back to silver chromate by treatment with silver nitrate solution and the process repeated; 2AgCl are added per cycle [7]:

$$CrO_4^{2-} + 2Ag^+ \rightarrow Ag_2CrO_4$$

$$Ag_2CrO_4 + Ba^{2+} + Cl^- \rightarrow BaCrO_4 + 2AgCl$$

$$BaCrO_4 + 2Ag^+ \rightarrow Ag_2CrO_4 + Ba^{2+}$$

This can be represented as a cycle (Scheme 3).



Scheme 3

Thus after going through the cycle n times, the amount of material for measurement is $Ag_2CrO_4 + n(2AgCl)$ based on 1 mole of CrO_4^{2-} (or $2Ag^+$) initially present. Amplification is by way of n additions of material and is thus distinguished from direct multiplication, which after n cycles would produce K^n moles of the starting material.

Accuracy in repeated addition or accumulation reactions depends on the extent of complete removal of the excess of reagent used in the various ion replacement stages of the reaction cycles.

Enhanced equivalence reaction or enhanced factor reaction

This is a reaction where the analytical measurement is (or is deemed to be) more favourable than would be achieved if the same measurement had been applied directly (often possible in theory only). An example is the determination of iodide by reaction with hypochlorite [8]:

$$I^- + 3ClO^- \rightarrow IO_3^- + 3Cl^-$$

Because 1 mole of iodide consumes 3 moles of hypochlorite a more favourable redox titration factor (stoichiometric ratio) is achieved as compared to that given by the more usual reaction of iodine (formed by direct oxidation of iodide) with thiosulfate.

In many instances, although one intuitively feels that a more favourable measurement has been made, comparison with the unamplified method is meaningless. Thus no amplification factor should be defined or calculated in such instances. Another example is the determination of bismuth by precipitation as $Bi[Cr(SCN)_6]$, and titration of the thiocyanate in the precipitate with permanganate (manganate(VII)).

Molar mass enhancement reaction

An example of the gravimetric application of such a reaction is the determination of phosphate by weighing as ammonium 12-molybdophosphate (which is 142 times the weight of the original phosphorus) as compared to weighing as magnesium pyrophosphate (which is only 3.6 times the weight of the original phosphorus), a common weighing form for the gravimetric determination of phosphate. Relatively, more mass of material is available for weighing in the former instance, the increased factor being based on the stoichiometry of the reaction. This reaction is not an amplification reaction as defined earlier [2], and is best described by the term ‘molar mass enhancement reaction’.

Alternative element or ease of measurement amplification procedure

To describe the determination of phosphorus via the determination of the 12 associated molybdenum atoms in 12-molybdophosphate as a 12-fold amplification would only be true if the final measurement technique were equally sensitive per mole for both elements. If, for example, flame atomic absorption spectrometry were used for the measurements the overall increase in sensitivity for phosphorus determination based on molybdenum measurement is much greater than 12 since the sensitivity of the measurement technique is much higher for molybdenum than it is for phosphorus. A parallel situation applies with UV-visible spectrophotometric measurements where different reagents for a given analyte give different ‘ease of measurement’ arising from the different values for molar absorptivities. Such reaction measurement schemes may be termed as ‘ease of measurement’ or ‘alternative element amplification procedures’ if there is an increase in the number of atoms potentially available for final measurement.

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