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# CATALYTIC METHODS OF ANALYSIS: CHARACTERIZATION, CLASSIFICATION AND METHODOLOGY

(Technical Report)

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# Catalytic methods of analysis: Characterization, classification and methodology

*Synopsis*

Analytical methods based on the measurement of time changes in the concentrations of certain components of suitable reaction systems are very varied, differing both methodically and in application. This report presents a classification of kinetic methods based on the chemistry of the reaction employed.
Catalytic determinations are the most widely used of the kinetic methods. The field of catalytic methods includes the methods of determination of trace concentrations of metal ions, anions and many organic substances. Low detectable quantities and high sensitivities are recognised as major advantages of catalytic determinations. Selectivity, on the other hand, can be considered to limit the practical application of these determinations.

## INTRODUCTION

In recent years many catalytic methods have been studied. The evolution and the innovations introduced over the last two decades have been reviewed comprehensively [1-4]. The field has been reviewed biennially in Analytical Chemistry since 1964 [5] and a number of other reviews have also appeared [6-8].
The importance of kinetic studies goes beyond their direct application in determinations, since most physical or chemical processes used in contemporary analytical chemistry have their kinetic aspects. Mottola [3] has, for example, discussed systematically the aspects of kinetics that have become part of modern analytical chemistry. Every process, whatever its nature, takes place at a finite rate, tending to an equilibrium state. The two states, the kinetic (dynamic) state, and the equilibrium (static) state are both of "high informing power" [4]. Reaction-rate methods are becoming increasingly important practically in analytical chemistry; progress however relies heavily on better elucidation of the mechanisms of chemical reactions. Recent developments in instrumental design and, especially, in the incorporation of microcomputers for the control of experiments and data evaluation allow for improved precision, limits of detection, rapidity and automation of such methods.

## CLASSIFICATION OF KINETIC METHODS BASED ON THE CHEMISTRY OF THE REACTIONS EMPLOYED

The application of kinetic measurements in chemical analysis can be subdivided as follows:

**Homogeneous systems:**

o   Catalytic methods - determination of catalyst or activator/inhibitor
o   Non-catalytic methods
  -   Determination of a single species
  -   Determination of two or more species (commonly known as differential methods).
     Because of their special features, enzymatic methods are often classified separately.
o   Enzymatic methods - determination of enzymes, substrates or activators/inhibitors

**Heterogenous systems:**

o   Electrochemical methods (based on electrode reactions)
o   Methods employing immobilised enzymes
  - Determination of enzymes, substrates or activators/inhibitors

# CATALYTIC METHODS

Catalytic determinations are the most widely used of the kinetic methods. Using a catalytic reaction, one can determine extremely low concentrations of the catalyst through an increase in the reaction rate because a catalyst participates in a large number of cycles of the catalytic reaction. Increasing the concentration of the catalyst gives rise to a direct increase in the reaction rate.

Catalytic methods are in many cases as sensitive (see table 2) as luminescence methods, activation analysis methods and electrothermal atomic absorption spectrometry.

One of the main advantages of such methods is the possibility of determining traces, especially of anions and many organic substances, simply and rapidly, with very low detection limits. Procedures have been developed involving the use of simple glassware, a timing device and a thermostat. Most methods require a visible - range spectrophotometer but can be readily automated.

Catalytic determinations are generally based on either of the following two approaches:

(i) direct use of primary catalytic effects (determination of catalyst)
(ii) use of modified catalytic rates (determination of modifier such as an activator or an inhibitor)

The earliest known kinetic determination of a species on the basis of its catalytic effect was reported by Guyard [9], who in 1876 described the determination of vanadium through its catalytic effect on the oxidation of aniline by potassium chlorate. The history of kinetic methods of analysis has been summarised by Mottola [3].

## Indicator reactions and substances, methods of determination

The reaction catalyzed by the analyte is known as the "indicator reaction" [3,4]. There are at least 300 different indicator reactions documented for determining about 50 elements and numerous compounds [1-5]. An indicator reaction is always thermodynamically favoured, but kinetic factors may seriously hinder or, for all practical purposes, prevent the uncatalyzed reaction occuring within the time scale of experimental observation. The catalyst facilitates the process of converting reactants to products.

In most cases, the change in concentration of only one of the substances participating in a reaction is determined.

The substance by which the indicator reaction rate is monitored (monitoring species) is often called the "indicator substance" [1,8].

If we take a reaction such as

$$A + B \xrightarrow{k_u} P_1 + P_2 \qquad (1)$$
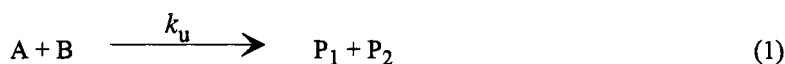
where $P_1$ and $P_2$ are the products formed by the uncatalyzed reaction of A with B, then assume that in the presence of a catalyst C, a new mechanistic pathway is set up as follows:

$$A + C \xrightarrow{k_c} P_1 + X \qquad (2)$$

$$X + B \xrightarrow{\text{fast}} P_2 + C \qquad (3)$$
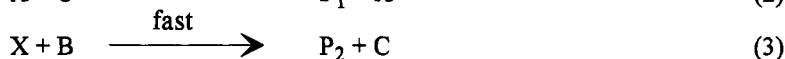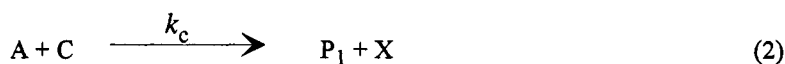
where X is a reactive intermediate then, if reaction (3) is much faster than reaction (2), the concentration of the catalyst will remain constant during an experiment and the reaction rate ($v$) will be the sum of the rates of the uncatalyzed reaction and the catalyzed reaction, i.e.

$$v = -\frac{d[A]}{dt} = k_u \cdot [A][B] + k_c \cdot [C][A][B] \qquad (4)$$

where A is the indicator substance.

The concentration of one reagent, say B, is usually arranged to be present at a much higher level than the other, so that its concentration also remains effectively constant during an experiment.

Assuming that the rate of the noncatalyzed reaction can be neglected, we have

$$v = -\frac{d[A]}{dt} = [C]_0 \cdot \varPi \cdot k_c \tag{5}$$

where $[C]_0$ is the concentration of the catalyst to be determined, $\varPi$ is the product of the concentrations of substances affecting the indicator reaction rate, and $k_c$ is the reaction rate constant. The overall rate law for a catalytic reaction may be obtained only after carefully investigating its kinetics. Therefore, one cannot estimate the concentration of a catalyst directly in all cases. For the determination of unknown concentrations of a catalyst calibration curves are necessary.

Two main approaches exist for data treatment in catalytic determinations, namely differential (derivative) and integral methods [3]:

A. **Differential methods:**

Direct evaluation of d (signal)/d$t$.

- Initial rate measurements, in which the initial reaction rate is determined and utilised for the evaluation of concentration.
- Slope measurements in which the slope of the response curve at a selected point is measured and related to the concentration

B. **Integral methods (or integration methods):**

Integral methods are based on the evaluation of the corresponding rate expressions over a finite, constant and normally small time interval $\Delta t$.

- Fixed time measurements, in which the change of a parameter, related to the concentration of a reactant or product, is measured over a predetermined time interval
- Fixed concentration or variable-time method, in which the period of time, required to bring about the same predetermined change in the concentration of a reactant or product, is measured

C. **Other methods:**

- Methods based on the measurements of the length of induction periods
- Special methods such as oscillating chemical reactions

Differential and integral methods are most frequently used for catalyzed reactions [8]. Detailed descriptions of methods for the determination of catalytically active substances and a discussion of accuracy and precision are given by Mottola [3] and Perez-Bendito and Silva [4].

It is very important to note that the precision of kinetic methods depends on the reliability of the analytical technique used to measure the changes in the concentration of a given component (indicator substance) as a function of time.

**Mechanisms of analytically important catalytic reactions**

Indicator reactions for catalytic (non enzymatic) methods may be classified on the basis of reaction mechanisms as follows [6]:

A. **Redox reactions**

1. With valency change of the catalyst
2. Without valency change of the catalyst

B. **Exchange reactions with coordination compounds**
   1. Nucleophilic substitution
   2. Electrophilic substitution
   3. Coordination chain reactions
C. **Reactions with carbonyl compounds**
   1. Hydrolysis reactions
   2. Decarboxylation reactions

Knowledge about the mechanisms of the reaction is far more important for catalytic methods than for methods based on chemical equilibrium. In the latter procedures, in most cases, proportionality between the concentration of the substance to be determined and one parameter of the reaction at equilibrium is sufficient for analytical purposes, regardless of the stage of reaction at which the equilibrium is attained. The more knowledge is obtained on the mechanism of a catalytic reaction, the more easily one will find the most favourable conditions for analytical applications of the reaction with regard to sensitivity, accuracy, and selectivity.

**Redox reactions**

The most common indicator reactions are redox in nature and involve oxidants such as $H_2O_2$, $O_2$, $BrO_3^-$, $ClO_3^-$, $IO_3^-$, $IO_4^-$, $S_2O_8^{2-}$, $Fe^{III}$, $Ce^{IV}$, etc., and inorganic reductants such as $Sn^{II}$, $Fe^{II}$, $As^{III}$, $S_2O_3^{2-}$ and organic reductants such as amines, phenols, azo dyes and leuco bases of dyes, etc. [8]. Redox reagents can be classified into two main groups, namely, reactants acting by electron transfer through their d-orbitals and reactants acting by electron transfer through their s- and p-orbitals (see table 1). Reactions with oxidants of the second group are as a rule slower than those of the first group and thus are convenient as indicator reactions for determining catalytically active substances.

Table1: Typical Oxidising and Reducing Agents Used for the Determination of Catalysts

| | Oxidising Agents | | | | Reducing Agents | | | |
|---|---|---|---|---|---|---|---|---|
| d-orbitals | $Ce^{4+}$ | $Cu^{2+}$ | $Ag^{2+}$ | $Mn^{3+}$ | $Cr^{2+}$ | $Fe^{2+}$ | $Ti^{3+}$ | |
| | $Fe^{3+}$ | $VO_2^+$ | $MnO_4^-$ | | $V^{3+}$ | $VO^{2+}$ | | |
| | $CrO_2^{2+}$ | $MoO_2^{2+}$ | $OsO_4$ | | | | | |
| s,p-orbitals | $Sn^{4+}$ | $Sb^{5+}$ | $Pb^{4+}$ | $Bi^{5+}$ | $I^-$ | $Sn^{2+}$ | $Br^-$ | $Cl^-$ |
| | $Tl^{3+}$ | | | | $N_3^-$ | | | |
| polyatomic species | $H_2O_2$ | $NO_3^-$ | $ClO_3^-$ | $ClO_4^-$ | ArOH, ArNH$_2$, azo dyes, | | | |
| | $BrO_3^-$ | $S_2O_8^{2-}$ | $IO_4^-$ | | leuco bases of dyes, | | | |
| | | | | | $AsO_2^-$, $S_2O_3^{2-}$, $C_2O_4^{2-}$, | | | |
| | | | | | ascorbic acid | | | |

The reactions can be divided into two groups, depending on whether the ion acting as the catalyst changes its oxidation state during the reaction or not.

Reactions in which the oxidation state of the ion-catalyst changes are marked by high sensitivity. Catalyst concentrations from $10^{-9}$ to $10^{-7}$ g cm$^{-3}$ may be commonly determined and in some cases

(Co, Os, Ru) down to $10^{-11}$ g cm$^{-3}$ [4, 6]. The mechanism of reactions of this type involves the steps

$$Red + C^{(n+1)+} \longrightarrow P + C^{n+} \tag{6}$$

$$C^{n+} + Ox \longrightarrow C^{(n+1)+} + Z \tag{7}$$
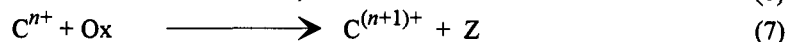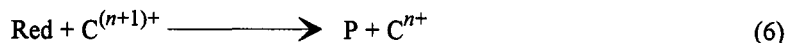
where $C^{(n+1)+}$ and $C^{n+}$ are the two different valency forms of the catalyst in the two oxidation states, Red and Ox are the reactants in the redox reaction and P and Z are the reaction products. In these reactions, ions of the transition elements and halides usually function as catalysts.

The other large group of catalytic redox reactions comprises the reactions in which the oxidation state of the ion-catalyst remains unchanged. These include catalytic oxidations by hydrogen peroxide in acidic medium. Catalytic activity is exhibited by cations with high positive charges that readily form peroxocomplexes (e.q. $Fe^{III}$, $Ti^{IV}$, $Hf^{IV}$, $Th^{IV}$, $V^V$, $Nb^V$, $Ta^V$, $Cr^{VI}$, $Mo^{VI}$ and $W^{VI}$).

Generalised overviews of the mechanism of catalytic reactions of analytical interest have been given by Bontchev [10] and by Mottola [3].

**Reactions with carbonyl compounds and catalytic ligand exchange reactions**

These catalytic reactions include catalytic decompositions, hydrolysis and catalytic substitution reactions of both organic and inorganic substrates [10].

The reactions are analytically important, because they are often catalyzed by elements from the main groups of the periodic table whose ions have no vacant d-orbitals and thus cannot catalyze redox processes.

The mechanism of catalysis by catalytic decomposition and hydrolysis involves the effect of the catalyst on the polarization of the bonds in the reactants or on the orientation of the reactants, thus making the reaction possible. An important step in the catalysis is then often chelation: the ions of the catalyst form stable chelates with the substrates. An example is the hydrolysis of monoalkyl phosphates $ROPO_3^{2-}$. These substances alone do not hydrolyze in alkaline media. In the presence of $Cu^{2+}$ or $Mg^{2+}$ ions, neutral chelates are formed, the negative charge on the substrate is neutralized and hydrolytic decomposition can begin.

From the analytical point of view, catalytic substitution reactions of complexes are also important [2]. Typical reactions of this type are the substitution reactions of hexacyanoferrate(II) with water, bipyridine or phenanthroline, represented in a simplified form as

$$[Fe(CN)_6]^{4-} + X \longrightarrow [Fe(CN)_5X]^{3-} + CN^- \tag{8}$$
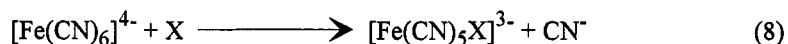
where X: water, bipyridine or phenanthroline.

Reaction (8) is catalyzed by all metal ions that form stable complexes with cyanide (e.g. mercury, silver, gold) and can be used to determine these metals [11]. Other methods based on ligand - exchange reactions are quite recent and have thus been studied less. They have a promising future as they allow the determination of non-transition metals such as alkaline-earth metals as well as of lanthanides, ammonia and some other species. Three general types of ligand - exchange reaction can be considered in this context, as follows [2,4]:

**Exchange of a ligand between two metal ions:**

The system

$$NiY^{2-} + Zn^{2+} \rightleftharpoons ZnY^{2-} + Ni^{2+} \tag{9}$$

has been described by Margerum et al. [12]. This reaction moves slowly and is monitored photometrically at 380 nm by measuring the disappearance of the $NiY^{2-}$ - complex. The addition of a small amount of $Cu^{II}$ to the system results in two further reactions:

$$NiY^{2-} + Cu^{2+} \longrightarrow CuY^{2-} + Ni^{2+} \tag{10}$$

$$CuY^{2-} + Zn^{2+} \longrightarrow ZnY^{2-} + Cu^{2+} \tag{11}$$
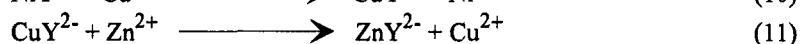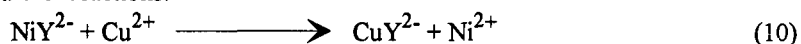
The $CuY^{2-}$ complex is rapidly formed, immediately reacts with zinc ions to form the $ZnY^{2-}$ complex and the $Cu^{2+}$ ions are liberated. $Cu^{II}$ ions are thus not consumed and can be considered as catalyst. Copper ions can be determined on this basis.

**Exchange of a metal between two ligands:**

Consider the reaction between $Cu^{II}$ and the ligands oxybis(ethylenenitrilo) tetra-acetic acid (EGTA) and 4-(2-pyridylazo)resorcinol (PAR)

$$Cu\text{-}EGTA + PAR \longrightarrow Cu\text{-}EGTA \qquad (12)$$

This reaction is catalyzed by traces of $Ca^{II}$. $Mg^{II}$ causes no interference, as its EGTA complex is much less stable than that formed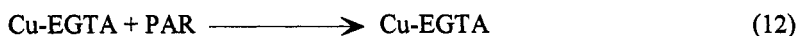 with $Ca^{II}$. Calcium ions can thus be determined at concentrations between 0,4 and 40 $\mu g\ cm^{-3}$ by spectrophotometrically monitoring (at 515 nm) the rate of appearance of the Cu-PAR complex [13].

**Dual exchange reactions (coordination chain reactions)**

Olsen and Margerum [14] have found, that complex ligand exchange occurs in the reaction of Cu-EDTA with Ni-trien

$$NiT^{2+} + CuY^{2-} \longrightarrow CuT^{2-} + NiY^{2-} \qquad (13)$$
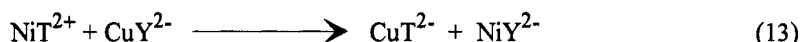
where   T = trien = triethylentetramine

This reaction develops very slowly, though it can accelerated by simply adding an excess of one of the ligands. Thus, a small excess of EDTA ($Y^{4-}$) attacks the Ni-trien complex to yield Ni- EDTA and free trien (T), which in turn reacts with the Cu-EDTA complex, from which it displaces the ligand:

$$Y^{4-} + NiT^{2+} \longrightarrow NiY^{2-} + T \qquad (14)$$

$$T\ \ + CuY^{2-} \longrightarrow CuT^{2+} + Y^{4-} \qquad (15)$$
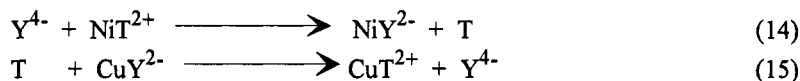
The chain is propagated cyclically and a steady state is rapidly reached. The reaction rate is monitored photometrically by means of the absorbance at 550 nm, which corresponds exclusively to the Cu-trien complex and is proportional to the EDTA (or trien) concentration added. This allows the determination of small concentrations of ligand. Metal ions can act as an inhibitor for the ligand-catalyzed reaction. In this way, trace concentrations ($10^{-7}$ to $10^{-10}$ g cm$^{-3}$) of metals forming stable complexes with, e.g., EDTA can be determined. Other examples for the analytical use of substitution reactions are described by Kopanica et al. [15-17].

**Application of oscillating reactions**

This type of reaction has limited but increasing analytical interest [18]. Reactions catalyzed by metal ions capable of exchanging a single electron at normal potential values between 0.9 and 1.6 V (e.g. the $Ce^{IV}/Ce^{III}$ system) are typical representatives of oscillating reactions, as are the $Ce^{IV}$-catalyzed oxidation of malonic acid (Belousov-Zhabotinski reaction system, B.-Z. system), succinic acid or citric acid by bromate.

Mechanistically these processes are very complex. For the bromate-malonic acid reaction catalyzed by $Ce^{IV}$ - $Ce^{III}$, a 10-step process for the mechanism has been proposed [18,19,20]. The process (e.g. B.-Z. system) is monitored either by photometric measurement of the changes in the $Ce^{IV}$ concentration or by non-equilibrium measurements of the redox potential of the $Ce^{IV}/Ce^{III}$ pair, which shows the periodic variation of the $Ce^{IV}$ concentration, or by using a bromide-selective electrode.

It is analytically important that the number of cycles per unit of time is proportional to initial reactant concentrations. However, this relationship is only obeyed closely for a short time after the initiation of the

reactions; when reagent concentrations decrease, so does the cycle frequency. An example of such use is the determination of ruthenium based on the increase of the period frequency in the oxidation of malonic acid catalyzed by cerium in presence of the $Ru^{III}$ - $Ru^{IV}$ redox couple [20].
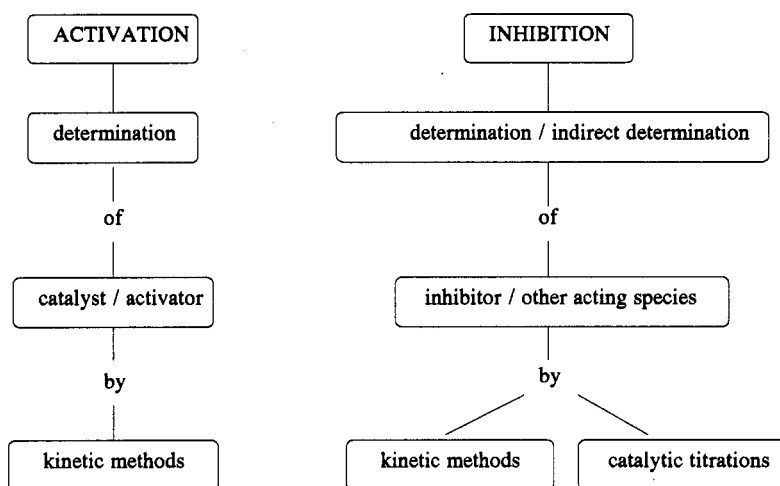
As little as 0,01 $\mu g$ $cm^{-3}$ Ru can be determined with excellent reproducibility, and small concentrations of Pt, Rh, and Ir do not interfere.

The kinetic determination of hexacyanoferrate ($7 \cdot 10^{-8}$ - $7 \cdot 10^{-6}$ mol $dm^{-3}$) by its inhibition of an oscillating chemical reaction (B.-Z. system) was described by Jiang et al. [21].

**Methods based on modified catalyzed reaction rates**

Such methods involve interactions of a given chemical species with a catalyst so as to prevent it from entering the catalytic cycle (inhibition) or to produce a chemical species reacting through a path of lower activation energy (activation).

The major impact of developing methods based of modification of catalytic reaction rates is the determination of organic species, especially in connection with environmental problems. Analytical aspects of the use of effects modifying the rate of a catalyzed reaction are shown in the following scheme:

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      ┌──────────────┐                 ┌──────────────┐
      │  ACTIVATION  │                 │  INHIBITION  │
      └──────┬───────┘                 └──────┬───────┘
      ┌──────┴───────┐        ┌──────────────┴──────────────┐
      │ determination │        │ determination / indirect determination │
      └──────┬───────┘        └──────────────┬──────────────┘
             of                               of
      ┌──────┴───────┐        ┌──────────────┴──────────────┐
      │ catalyst /   │        │ inhibitor / other acting    │
      │  activator   │        │         species             │
      └──────┬───────┘        └──────────────┬──────────────┘
             by                        ┌──── by ────┐
      ┌──────┴───────┐        ┌────────┴─────┐  ┌────┴──────────┐
      │kinetic methods│        │kinetic methods│  │catalytic titrations│
      └──────────────┘        └──────────────┘  └───────────────┘
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Nitrilotriacetic acid (NTA) is probably the most commonly determined activator. This acts upon the $Mn^{II}$-catalyzed reactions of periodate with malachite green or phosphinate or $Sb^{III}$, respectively, and has been determined at concentrations of the order of $10^{-6}$ mol $dm^{-3}$ by the fixed concentration method [23].

Other examples are the determination of ascorbic acid (activation of the $V^{V}$-catalyzed reaction between I⁻ and $ClO_3^-$) and of citric acid (activating effect on the reaction between ferroin and $Cr^{III}$).

Most of the kinetic methods for the determination of inhibitors involve a reaction with the catalyst (generally complex formation) which hinders the catalytic cycle [24]. The complex either exerts less catalytic action than the free metal ion (partial inhibition), or complexation renders the catalyst completely inactive (total inhibition). In either case the effect on the reaction rate will be proportional to the concentration of the inhibitor and can be used for its determination.

Titrimetric endpoint detection is a major application of the inhibitory effect in catalyzed reaction. The possibility of using catalyzed reactions for end-point detection in titrations was originally proposed by Yatsimirskii and Fedorova [25]. Such titrations are based on the inhibitory effect of a substance (whether an anion, ligand or metal) on a metal- or anion-catalyzed reaction and are applied to the determination not
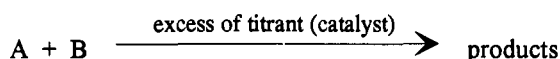
only of the inhibitor, but also of the catalyst or other species (generally metal ions) with no catalytic or inhibitory properties [4]. The approach involves the use of two consecutive reactions:

(a)  the titration reaction, in which a catalytic titrant added to the sample reacts rapidly and stoichometrically with the sought-after species (the inhibitor) and

(b)  the indicator reaction, which involves the monitored species and, under given conditions, can occur at a noticeable rate only when an excess of catalyst (titrant) is present in the system [3].

Titration reaction

$$\text{titrant (catalyst)} + \text{analyte (inhibitor)} \longrightarrow \text{products}$$

indicator reaction

$$A + B \xrightarrow{\text{excess of titrant (catalyst)}} \text{products}$$

The endpoint is detected by the sudden increase or decrease of the rate of the indicator reaction, and the amount of the catalyst needed to reach the endpoint is directly proportional to the amount of the inhibitor present in the sample.

A description and the theoretical background has been given of the complexometric [26], redox and precipitation [27], and acid-based reactions [28] as well as the nature of the titration curves with catalytic endpoint indications [29] and catalytic titrations involving thermometric detection [30].

**Sensitivity and limits of detection in catalytic determinations**

Low detection limits (lowest concentration of catalyst measured with high probability, usually defined as 2 or 3 time the standard deviation of the blank) and high sensitivities (represented by the slope of the calibration graphs) are recognised as major advantages of catalytic determinations.

The high sensitivity of the catalytic methods can easily be explained in the following way:

Replacing infinitely small changes by increments in eq. 5 we obtain

$$[C]_0 = - \frac{\Delta[A]}{\Delta t} \cdot \frac{1}{k_c \cdot \Pi} \tag{16}$$

If the change in [A] is followed spectrometrically (as is commonly done), we can assume, that the lowest measurable change in A, $\Delta[A]$, is equal to about $10^{-7}$ mol dm$^{-3}$. If the time required to complete the test, $\Delta t$, does not exceed 10 minutes and the rate coefficient is of the order of $10^4$ min$^{-1}$ then we can estimate that under these conditions ($\Pi$ about 1 mol dm$^{-3}$) $[C]_{0\ min} = 10^{-12}$ mol dm$^{-3}$.

The limit of detection of the catalytic methods also depends on several factors discussed below.

In the first place, apart from the catalytic reaction a noncatalytic process may also occur due to the presence of impurities in the system.

The total reaction rate, therefore, is the sum of the two rates:

$$v_{total} = v_{cat} + v_{background}$$

The rate of the catalytic reaction is found to be the difference between the total reaction rate and the rate of any noncatalytic reaction. Thus one should keep the background conditions as constant as possible.

Catalyst concentrations within the range $10^{-6} - 10^{-11}$ g cm$^{-3}$ can usually be determined. Table 2 lists the elements that have been determined on the basis of their catalytic activity and the corresponding minimum determinable concentrations. It can be seen that over 40 elements have been determined with low detection limits.

Limits of detection are often overemphasised as advantageous in catalytic determinations; lack of selectivity, on the other hand, can limit the practical applications of these determinations [31].

**Selectivity of catalytic methods of analysis**

According to IUPAC terminology [32], selectivity denotes the extent to which the method is free of interference by other chemical species. Total or complete specifity is the case in which no interferent effects are known. In practice total specifity is rare for catalytic methods apart from enzyme-catalyzed reactions. The catalytic properties of an inorganic ion depends on its size, structure, charge and coordination sphere; chemically similar species exhibit similar catalytic effects, and therefore highly selective catalytic determination in the presence of chemically related elements is not common. Consider the indicator reaction

$$A + B \longrightarrow P \tag{17}$$

which takes place in the presence of catalyst C at a rate defined by the equation

$$v = \frac{d[P]}{dt} = k' [A]^{p'} [B]^{q'} + k [A]^{p} [B]^{q} [C] \tag{18}$$

where A, B are the reactants, $k'$, $k$ are the rate constants for the uncatalyzed and the catalyzed reaction, respectively, and symbols $p'$, $q'$, $p$, and $q$ are, in a simple case, the stoichiometric coefficients. In the presence of different catalysts $C_1$, $C_2$, ... , $C_n$ the expressions for the rate of the catalyzed reaction under different reaction conditions can be described by the equations (19, 20):

$$v_1 - v_{10} = k_{11} \, \Pi_{11} \, [C_1] + k_{12} \, \Pi_{12} \, [C_2] + ... + k_{1n} \, \Pi_{1n} \, [C_n] \tag{19}$$

$$v_n - v_{n0} = k_{n1} \, \Pi_{n1} \, [C_1] + k_{n2} \, \Pi_{n2} \, [C_2] + ... + k_{nn} \, \Pi_{nn} \, [C_n] \tag{20}$$

where $v_1$,..., $v_n$ characterise the rates of the catalyzed reaction; $v_{i0}$ the rates of the uncatalyzed reaction and $\Pi_{ik} = [A]^{pik}[B]^{qik}$, where $i$, $k = 1, ..., n$, the coefficients $p$, $q$, ... are determined by the actual mechanism. For the activity of a certain catalyst to be highly selective, the activities of the individual catalysts must differ considerably. Under the given reaction conditions, $k_{ii} \neq k_{ik}$ or, the individual catalysts must react according to different reaction mechanisms i.e. $p_{ii}$, $q_{ii} \neq p_{ik}$, $q_{ik}$.

The selectivity of a catalytic determination can often be improved by optimizing the procedure by selective masking or by using separation techniques.

The following scheme shows ways to improve the selectivity of catalytic methods

| **Optimisation of the procedure** | **Use of separation techniques** |
|---|---|
| o   Variation of reaction conditions | o   Ion-exchange |
| -   pH | o   chromatographic methods |
| -   reagent concentration | o   microdiffusion |
| -   temperature | o   co-precipitation |
| -   suitable co-ordination sphere | o   distillation |
| -   catalyst-substrate interaction | o   electrophoresis |
| -   photoactivation | o   liquid-liquid-extraction |
| o   mechanism-optimisation | -   back-extraction or |
|      (e.g. by means of the graph method) |      composition of the organic solvent |
| | -   extraction-catalytic determinations |

If a suitable masking agent is not available, the selectivity of a catalytic reaction can be improved only by the separation of interfering ions. Separation techniques known from other forms of trace analysis are suitable; examples are given in table 3 .

Table 2 :

Survey of the elements which can be determined using the catalytic activity of their ions. The numbers beside the symbols of the elements denote the detection limit expressed as the negative logarithm of the corresponding concentration in $g\ cm^{-3}$ (according to [4-6])

| Ia | IIa | IIIb | IVb | Vb | VIb | VIIb | VIIIb | | | Ib | IIb | IIIa | IVa | Va | VIa | VIIa |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | |
| Li | Be 9 | | | | | | | | | | | B | C | N | O | F 10 |
| Na | Mg 6 | | | | | | | | | | | Al 6 | Si 6 | P 8 | S 10 | Cl 7 |
| K | Ca 6 | Sc | Ti 8 | V 10 | Cr 9 | Mn 10 | Fe 9 | Co 11 | Ni 9 | Cu 11 | Zn 9 | Ga | Ge 7 | As 5 | Se 9 | Br 8 |
| Rb | Sr | Y 7 | Zr 8 | Nb 7 | Mo 10 | Tc 8 | Ru 11 | Rh 10 | Pd 9 | Ag 10 | Cd 6 | In 8 | Sn | Sb 8 | Te 10 | I 10 |
| Cs | Ba | La | Hf 7 | Ta 7 | W 10 | Re 9 | Os 11 | Ir 11 | Pt 7 | Au 9 | Hg 9 | Tl | Pb 8 | Bi 7 | Po | At |
| Fr | Ra | Ac | Th 7 | Pa | U 9 | | | | | | | | | | | |

Table 3: Combination of catalytic analytical procedures with separation methods [1, 31]

| Element or compounds | Indicator reaction | Separation system or technique | Matrix |
|---|---|---|---|
| **Liquid-liquid extraction** | | | |
| Ni | diphenylcarbazone + tiron + $H_2O_2$ | dibenzylglyoxime / $CHCl_3$ | oxides of La, Y, P |
| Co | Alizarin S + $H_2O_2$ | 2-nitroso-1-naphthol | P |
| Au | $Hg^I + Ce^{IV}$ | HCl / ethyl acetate | ores |
| V | $p$-hydrazinobenzene-sulfonic acid + $ClO_3^-$ | oxine / $CHCl_3$ | blood, urine |
| Cr | 3,3'-dimethoxybenzidine + $H_2O_2$ | HCl / MIBK | $AlCl_3$ |
| Mn | $H_2O_2$ decomposition, 1,10-phenanthroline as activator | PAN / $CHCl_3$ | alkali metal halides |
| **Ion-exchange** | | | |
| Mo | $Fe^{III} + SnCl_2$ | Dowex 1, X-8 | sea-water |
| Se | Methylene Blue + $S_2^-$ | Dowex 50W-X2 | |
| Cr | 3,3'-dimethoxybenzidine + $H_2O_2$ | Dowex 50W-X8 | industrial atmosphere |
| Mn | Malachite Green + $IO_4^-$ | Amberlite CG-120 | Ta, Nb |
| **Chromatographic and other methods** | | | |
| F | zirconium-catalyzed reaction between perborate + $I^-$ (inhibiting action) | microdiffusion | biological material |
| Ru | benzidine + $H_2O_2$ | paper chromatography | aqueous solutions |
| I | $Mn^{II} + BrO^-$ | thin layer chromatography | |
| Cu | $Fe(SCN)_3 + S_2O_3^{2-}$ | co-precipitation on $Hg_2S$ | $Me^{II, III}$ salts |
| Ru | 3,3'-dimethoxybenzidine + $IO_4^-$ | distillation as $RuO_4$ | ores |
| dithio-carbamates | $N_3^- + I_2$ | high-voltage electrophoresis | aqueous solutions |

Liquid-liquid extraction is of greatest importance, followed by ion-exchange and other chromatographic methods. In extraction separations the simplest procedure preferable; in other words back-extraction or the thermal decomposition of the organic solvent should be avoided. It is advantageous to carry out the catalytic determination directly in the extract or in the extract dissolved in a mixed solvent (extraction - catalytic determinations) [31].

The following conditions must be satisfied to enable an extraction - catalytic determination:

(i)   the indicator reaction must proceed in the organic or mixed solvent and the catalyst activity must be retained in this medium,

(ii)  an extraction system must be available for a highly selective separation of the test metal and the extraction agent, if extracted itself, must not interfere with the catalytic reaction.

Extraction-catalytic methods are very attractive analytically, because they also enable analyses in very complex matrices. Table 4 gives an overview of extraction-catalytic methods that have been developed and used until the present time.

The nomeclature of kinetic methods of analysis (terms and definitions) is proposed in an IUPAC paper by Svelha [33].

Table 4 : Extraction-catalytic determinations [1]

| Metal Ion | Indicator reaction | Extraction System | Reaction Medium |
|---|---|---|---|
| Ag | Bromopyrogallol Red (BPR) + $S_2O_8^{2-}$ +1,10-phenanthroline | 1,10-phenanthroline, BPR / nitrobenzene | nitrobenzene-dioxan-water |
| Cu | sulphanilic acid + $H_2O_2$ + pyridine | pyridine, salicylate / $CHCl_3$ | $CHCl_3$-cthanol-watcr |
| | $p$-ethoxyaniline + $H_2O_2$ | neocuproine / $CHCl_3$ | $CHCl_3$-ethanol-water |
| $Cr^{VI}$ | 3,3'-dimethoxybenzidine + $H_2O_2$ | HCl / MIBK | MIBK-ethanol-water |
| Fe | $p$-ethoxyaniline + $H_2O_2$ + 1,10-phenanthroline | LiCl / MIBK | MIBK-ethanol-water |
| | $p$-ethoxyaniline + $H_2O_2$ + 1,10-phenanthroline | several systems | $CHCl_3$-ethanol-water |
| | $p$-ethoxyaniline + $H_2O_2$ + 1,10-phenanthroline | 1,10-phenanthroline, $CHCl_3$ | $CHCl_3$-ethanol-water |
| Mo | 1-naphthylamine + $BrO_3^-$ | oxine / $CHCl_3$ | $CHCl_3$-ethanol-water |
| Nb | $o$-aminophenol + $H_2O_2$ | benzoin oxime / $CHCl_3$ | $CHCl_3$-ethanol-water |
| Ti | $o$-phenylenediamine + $H_2O_2$ | pyrocatechol, dioctyl-amine / butanol | $CHCl_3$-ethanol-water |
| V | $o$-phenylenediamine + $BrO_3^-$ | pyrocatechol, octyl-dimethylamine / butanol | butanol-ethanol-water |

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