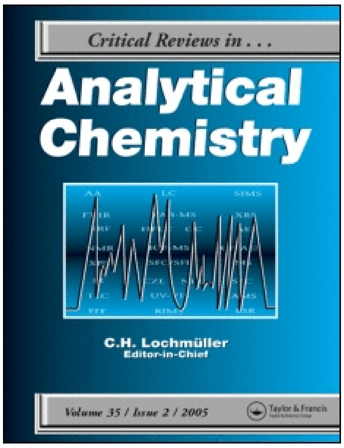

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CATALYMETRIC METHODS OF ANALYSIS

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I. INTRODUCTION

Analytical chemistry, apart from its original task of controlling chemical processes, confirming syntheses, or analyzing chemical products for their quality, within the last 20 years has been concentrating more and more on the problems and methodical possibilities of detecting and determining extremely small traces of elements and compounds. The importance of trace elements in all spheres of life and technology, which is generally accepted today, demands determination of those elements in various materials.

In biochemistry, trace elements are those elements which are required only in small amounts but are of vital necessity, whereas in geochemistry this term is applied for elements occuring at low levels of concentration in the earth's crust. Based on these concepts, a trace is generally understood as a very small amount of a substance that induces certain effects as well as other components present in excess, and whose detection is desired. Contents below $10^{-2}\%$ are called trace amounts. The concentration ratio between the main component and a trace amount is at least 10^4, and in extreme cases up to 10^{10} or over 10^{12}.

As regards the present status of trace analysis there are two predominant strategies, one physically and the other chemically orientated. The physically orientated school prefers direct instrumental techniques (activation analysis, optical emission spectroscopy, solid state mass spectroscopy, secondary ion mass spectroscopy, etc.), whereas the chemically oriented techniques are based on chemical reactions.

A direct instrumental technique is often preferred in comparison to a technique consisting of several individual steps, because it is less time-consuming, fewer human error sources are involved, and data processing is generally simpler. Direct instrumental analysis, however, offers several problems. Determination of element traces may be disturbed by the sample matrix, the resolution of the method may be not adequate, or there may be no sample standards available. Also, the main field of classical trace analysis has, within recent years, shifted from analysis in high purity solids, which were at the center of attention during the development of nuclear and semiconductor technology, to analysis of other materials whose importance has been rising due to pollution control and in connection with the developments in medicine, biology, and geology. Procedures of chemical determination are therefore of importance in trace analysis, even if they are frequently laborious, consisting of several steps and representing solution procedures almost exclusively. Moreover, many physical methods which are based, e.g., on atomization of the objects of investigation, are not suitable for analysis of organic substances. They are of little use in the field of anion analysis either, which is gaining more and more importance. In particular, they do not permit any distinction of the chemical individuality of the species to be determined (i.e., speciation). The latter aspect, however, is of increasing importance when considered from the point of view of biochemistry and pollution control.

As regards sensitivity, demands on the efficiency of trace-analytical methods of determination are growing. With high-purity materials, in particular high-purity metals determination of concentrations in the range of 10^{-10} to $10^{-12}\%$ is being discussed. Apart from determination of the total impurity content in a sample, it is also important to find out the local distribution of elements in and on the samples (distribution analysis). These problems can only be solved with applications of specially developed techniques for extreme traces. Figure 1 shows the growing demands on the efficiency of analytical methods as regards concentrations to be determined.

Currently, analytical chemistry has at its disposal procedures to meet these demands. Table 1 shows a selection of the most important trace-analytical procedures of determination and their analytical efficiency.

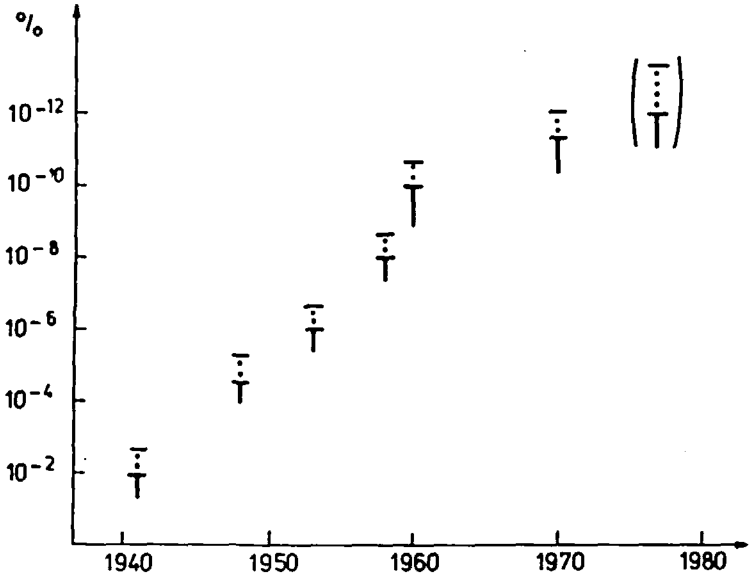


FIGURE 1. Requirements for procedures of analysis. (according to Alimarin[1]) —┤ achieved; ··┤ demands. (According to Alimarin, I. P., *Chem. Anal. (Warsaw)*, 19, 715 (1974). With permission.)

In some of the methods listed in Table 1 (gravimetry, volumetric analysis, spectrometry, fluorimetry, polarography, and catalymetry) a chemical reaction is needed to attain the detection limits listed.

After a period of almost exclusive utilization of physical effects in trace analysis and extensive instrumentation in analysis, which led to the frequently quoted statement of Liebhafsky,[3] "Like it or not, the chemistry is going out of Analytical Chemistry", the importance of chemistry and thus of chemical reactions[4] has been increasing in analysis (see also Werner[456]).

The chemical reactions used in analytical chemistry may be considered either in the state of equilibrium or in a given moment in their course. Either possibility is shown in Figure 2.

As regards sensitivity, chemical methods of analysis are usually inferior to physical ones (cf. Table 1), as a larger amount of analyte is demanded in order to produce a measurable effect. Various attempts are therefore being made to obtain further improvement in the sensitivity for chemical methods. For trace analysis, spectrophotometry plays a particular role as regards its wide range of application (e.g.[5-7]). Sensitivity of spectrophotometry is naturally limited, as the value determining sensitivity, the molar absorptivity ϵ_{max} cannot exceed a maximum of $\sim 10^{-5}$ [$mol^{-1}l\ cm^{-1}$].[8,9] If the working parameters are properly selected, the range of application of spectrophotometric procedures extends from the micro- to the millimole range.[7]

Increases in sensitivity in spectrophotometry may be achieved either by improvement of apparatus and technique or by a change of the chemical reaction with the aim of increasing absorption capacity or the number of absorbing molecules. Improvement of apparatus and technique include

1. New concepts in the design of spectrophotometers, involving improvement of photometric accuracy ($\Delta A \geqslant 0.0001$)

Table 1
IMPORTANT TRACE-ANALYTICAL PROCEDURES OF DETERMINATION AND THEIR ANALYTICAL EFFICIENCY

Methods	Detection limit (−log g)
Gravimetry	5
Volumetric analysis	7
X-ray fluorescence	7
Spectrophotometry	8
Fluorometry	9
Inverse voltammetry	10
Flame atomic absorption spectrometry	10
Optical emission spectrometry	10
Optical emission spectrometry with ICP	11
Catalymetry	12
Furnace atomic absorption spectrometry	12
Chelate gas chromatography	12
Mass spectrometry	12
Activation analysis	13
Radio-isotope technique	15

Adapted from *Proc. 2nd Symp. Solid State Mater.*, Karl-Marx-Stadt, DDR, 1978.

2. Application of new working techniques, like dual-wavelength spectrophotometry[10,11] and derivative-absorption spectrophotometry[12]

Changes of chemical reaction include

1. Variation of absorbing species
   - A. Variation of the organic reagent with an effect on molar absorptivity (see also Savin[457])
   - B. Formation of ternary complexes — ternary complexes, in which two different ligands are coordinated to one metal ion, play an increasingly important role in analytical chemistry.[13-19] Toêi et al.,[20] for example, determined trace contents of iron in the form of a ternary complex iron (II), 4-chloro-2-nitrosophenyl, and rhodamine B. The complex has a molar absorptivity of $\epsilon_{max} = 9 \times 10^4$ [mol^{-1} l cm^{-1}] and thus is considerably more sensitive than other iron reagents (i.e., with bathophenanthroline $\epsilon_{max} = 2.2 \times 10^4$ and with ferrozine $\epsilon_{max} = 2.8 \times 10^4$ [mol^{-1} l cm^{-1}].).
   - C. Use of surfactants and micellar systems — the application of tensids for increasing the sensitivity of spectrophotometric procedures of analysis is becoming more and more important, although the theoretical background is yet to be fully explained. There are numerous articles on the application of micellar systems for modification of photometric methods. A relatively comprehensive review in this respect is given by Hinze.[22] Some photometric systems illustrating the advantages listed above are given in Table 2.[21]
2. Chemical amplification[23] — chemical amplification consists of reacting a substance with a reagent through a catalytic, cycling, or multiplication mechanism to generate a relatively large amount of product (for definition see also Fritsche and Weisz[24]). In this way, in principle, a trace concentration of an analyte may be caused

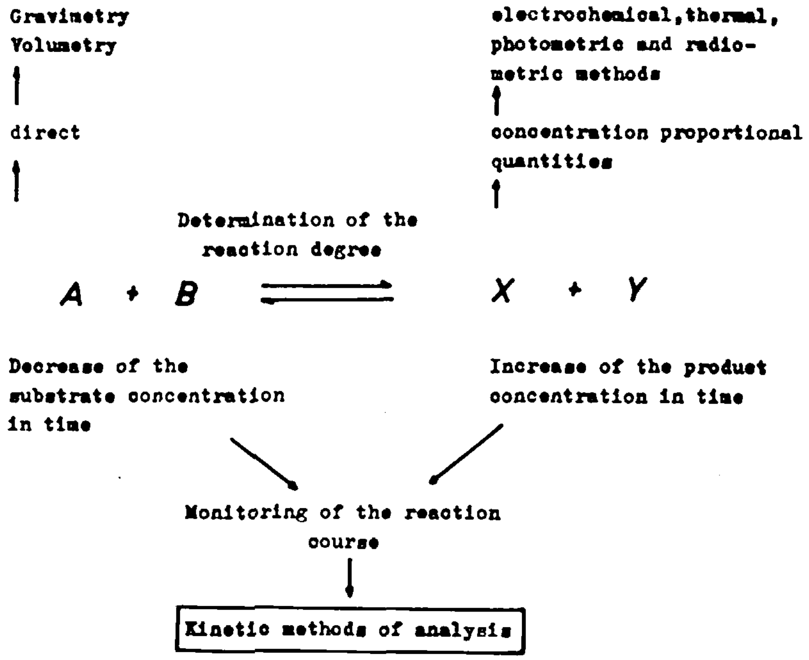


FIGURE 2. Chemical reaction as a source of analytical information.

Table 2
APPLICATION OF MICELLAR SYSTEMS FOR THE MODIFICATION OF PHOTOMETRIC METHODS

	λ_{max}		
Systems (conditions)	Reagent blank	Metal complexes	Metal complexes $0.10^{-4}\ \epsilon$ [l mol^{-1} cm^{-1}]
Fe(III)			
Chrome azurol S			
No micelles, pH 7		570	4.2
With CTMAC micelles, pH3,5[a]		630	14.7
Ti(IV)			
Disulfophenylfluoron			
No micelles, pH 6	500	570	10.8
With CPB micelles, pH 1[b]	470	620	12.8
In(III)			
Chrome azurol S			
No micelles		555	0.2
With CTAB micelles[c]		630	12.3
Sn(IV)			
Pyrocatechol violet			
No micelles		555	6.5
With CTAB micelles[c]		662	9.6

[a] CTMAC = cetyltrimethylammonium chloride.
[b] CPB = cetylpyridinium bromide.
[c] CTAB = cetyltrimethylammonium bromide.

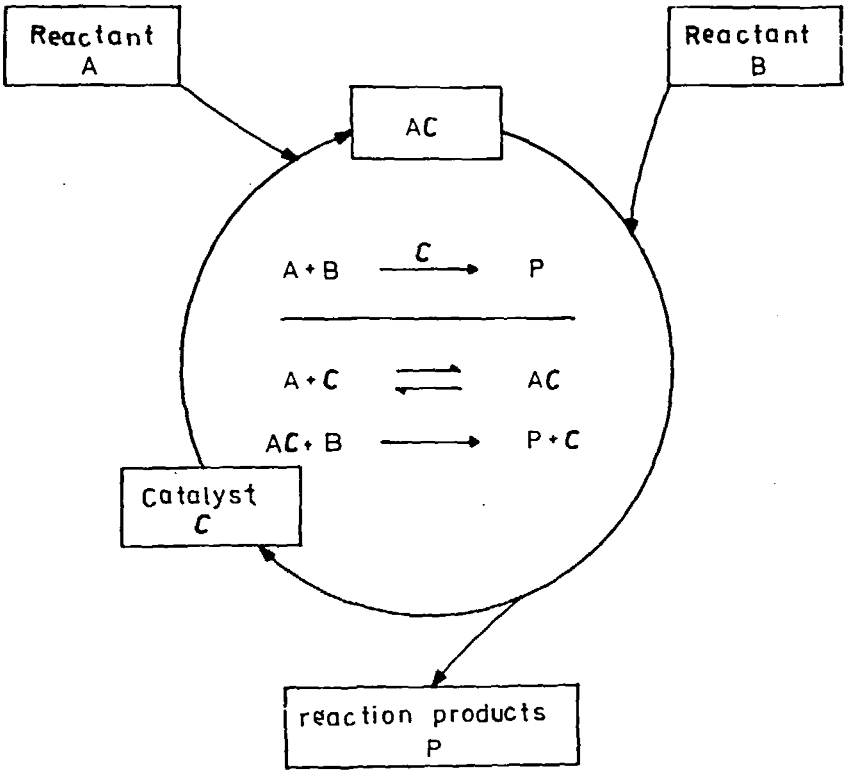


FIGURE 3. General catalytic cycle (determination of a catalyst C).

to yield order of magnitude higher product concentrations which, for analytical purposes, may be more easily measured than the analyte itself.[24,24a]

A generally applicable possibility for increasing the sensitivity of analytical procedures is the application of a catalytic cycle (see Figure 3).

As is commonly known, catalysts are substances which increase the rate of a chemical reaction by decreasing its activation energy and by forming active intermediate products, which are regenerated in the course of a reaction. Thus, multiples of reaction products are generated as compared with the stoichiometric amount of a catalyst. Therefore, large amounts of substance are obtained with small amounts of catalyst, which account for the extraordinarily high sensitivity of kinetic catalytic techniques.

As regards detection limits, the advantages of catalytic spectrophotometric techniques compared with equilibrium spectrophotometric techniques without amplification are given in Table 3 for some transition metals.[25-35]

II. KINETIC CATALYTIC METHODS OF ANALYSIS

A. Basic Remarks

If there is a definable correlation between the quantity of a physical phenomenon or measurement and the amount of substance causing this phenomenon, this functional correlation may be applied for determination of this substance. Basically, all measurable properties are applicable for this purpose.

In recent years more and more attempts have been made to get information on the

Table 3
COMPARISON OF THE DETECTION LIMIT (IN μg/mL) BETWEEN CATALYTIC SPECTROPHOTOMETRIC AND EQUILIBRIUM SPECTROPHOTOMETRIC TECHNIQUES

Element	Catalytic method	Ref.	Noncatalytic method	Ref.
Co	5×10^{-5}	26	2×10^{-3}	31
Cu	10^{-5}	27	1	32
Ni	10^{-3}	28	10^{-3}	33
Cr	10^{-5}	29	1	34
Mn	2×10^{-5}	30	1	35

quantity of a substance from observation of the time dependence of a reaction, i.e., kinetics (Figure 2, lower part).

The application of kinetics or rate measurements in analysis can be conveniently subdivided into four areas (see also Ottaway[458]):

1. Kinetic methods (i.e., noncatalytic) — determination of reactant
2. Catalytic methods — determination of catalyst or activator/inhibitor
3. Enzymatic methods — determination of enzyme, substrate, or activator/inhibitor
4. Differential reaction rate methods — determination of similar organic compounds in mixtures

Of these methods, enzymatic methods were described by other authors[134,421] and differential reaction rate methods by Mottola[38] in this journal in 1975.

The increasing frequency of application of kinetic catalytic procedures is due to better elucidation of reaction mechanisms with modern methods of investigation, further improvement of experimental techniques to follow the course of reactions (e.g., flow methods, relaxation methods, stopped-flow techniques and, in particular, the use of computers for processing of kinetic data.

At present, about 45 simple ions and a great number of various molecules can be determined by means of catalytic methods. Up to the mid 70s, however, use of catalytic methods of determination for practical analysis had been limited to a few special problems. Apart from widespread scepticism concerning measurements in dynamic systems, the following reasons account for this:

- Many of the suggested methods of determination were not thoroughly described as regards their practical applications (e.g., with regard to selectivity, sensitivity, accuracy, precision, and possibility of automation).
- Rather "exotic" (not commercial) compounds were suggested for indicator reactions.
- Precision and, in particular, selectivity as regards special requirements were often inadequate.

The papers which recently appeared in three selected journals have shown that this state-of-affairs is no longer a limiting factor and that catalytic determinations, formerly of more "academic" interest, have entered into the field of analytical practice (Table 4).

Table 4
PUBLICATIONS (1970, 1975, 1979) IN THE FIELD OF CATALYTIC METHODS OF ANALYSIS IN THREE SELECTED JOURNALS

	1970		1975		1979	
Journal	Sum	With application	Sum	With application	Sum	With application
Zh. Anal. Khim.	11	1	10	4	9	5
Anal. Chem.	2	—	1	1	5	3
Anal. Chim. Acta	1	—	5	1	7	4

B. Fundamentals of the Catalymetric Methods of Analysis

1. Indicator Reactions and Substances

The principle of catalytic or catalymetric methods of analysis is the measurement of the rate of chemical reactions whose course is accelerated by homogeneous catalysis. The component to be determined may act as a catalyst or, with indirect methods, as an inhibitor or activator. A chemical reaction whose change in rate is dependent on catalyst concentration and used for the determination of the amount of catalyst (activator, inhibitor) is called an indicator reaction.

In most cases, only the change of concentration of a substance (indicator substance) participating in a reaction is determined.

For a reaction accelerated by the catalyst K

$$A + B \xrightarrow{K} X + Y \qquad (1)$$

the reaction rate is

$$v = dc_X/dt = dc_Y/dt = (k + k_k\, c_K^{n_K}) \times c_A^{n_A} \times c_B^{n_B} \qquad (2)$$

where n_A, n_B n_K = order of reaction for the substrates and the catalyst, and k, k_k = constants of reaction rate for the noncatalyzed and catalyzed reactions, respectively.

As the reaction rate v and the catalyst concentration c_K are often directly proportional to each other ($n_K = 1$), the equation results in the following general function for kinetic (catalytic) determinations ($k \rightarrow 0$):

$$c_K = \frac{k'}{c_A^{n_A} \times c_B^{n_B}} \times v = \frac{k'}{c_A^{n_A} \times c_B^{n_B}} \times dc_X/dt \qquad (3)$$

where X is used as the indicator substance and $k' = k_k^{-1}$.

2. Methods for Determination of Catalytically Active Substances

(See also the detailed descriptions by Yatsimirskii[36,37] and Mottola.[38])

a. Evaluation of the Indicator Reaction

Differential variant — Degree of conversion may be neglected when concentrations of A and B are large; this condition is realized in initial rate methods.

Integral variant — Degree of conversion may not be neglected when compared with the original concentrations (c_o) of A and/or B.

Table 5
EVALUATING FUNCTION FOR THE DETERMINATION OF CATALYTIC CONCENTRATIONS

	Differential	Integral
Slope method (method of tangents)	$\Delta c_X/\Delta t \longrightarrow c_K$	$\Delta \ln c_A/\Delta t \longrightarrow c_K$
Fixed time (Δt = const.)	$\Delta c_X \longrightarrow c_K$	$\Delta \ln c_A \longrightarrow c_K$
Fixed concentration (Δc_X and $\Delta \ln c_A$, respectively = const.)	$1/\Delta t \longrightarrow c_K$	$1/\Delta t \longrightarrow c_K$

Note: Differential variant: $c_K = \Delta c_X/(\Delta t \cdot k_k \cdot c_{A_o} \cdot c_{B_o})$; integral variant: $c_K = \Delta \ln c_A/(\Delta t \cdot k_k \cdot c_{B_o})$; k_k = constant of reaction rate for the catalyzed reaction; Subscript o indicates initial concentration.

Both variants may use the slope method (method of tangents) of fixed time (single-point method) or method of fixed concentration (single-point method).

For reactions of the first order for the differential variants (with a reaction product X as the indicator substance) and for the integral variants (with an original substance A as indicator substance) the appropriate functional interrelations may be summarized in Table 5. Also, evaluation of the indicator reaction may be realized through an induction period ($c_K \rightarrow$ const./t_i or const./t_i^2,) according to the known-addition method.

b. *Comparative Methods*

As early as 1922 (Hahn, Ber., 55, 3070) and then in 1963 (Bognar[39]) a technique was suggested for the determination of the catalyst concentration, which is experimentally very simple. For this method of simultaneous comparison, the rate of the reaction containing the unknown amount of catalyst is compared with those of a number of "standard reactions" with known catalyst content under equal conditions. The main advantage of this technique is that conditions are exactly comparable as regards the course of experiment. Temperature variations may be neglected. Setting up the calibration curves and calculation of result is eliminated. For visual observation of the reaction, however, fairly large alterations of color intensities are necessary. According to several authors, errors in this variant of determination amount to ±10%. The reaction may also be observed spectrophotometrically, and the absorbance of several samples may be evaluated intermittently if so desired. By increasing the precision, the detection limit of catalytic determinations may be improved by almost one order of magnitude, e.g., in a catalytic determination of silver[40] from 1 ng to 0.2 ng Ag/mℓ, when the mechanized variant of the method of simultaneous comparison is used.

This comparative technique might gain importance for kinetic catalytic trace determination, as the recently developed centrifugal fast analyzers offer ideal conditions for this technique (simultaneous initiation of reaction in 20 to 30 samples under absolutely identical conditions). The so-called "difference" methods also belong to the comparative methods.[36,41]

c. *Application of Open Systems*[42,43]

Kinetic catalytic determinations are generally carried out in closed systems, in which a reaction is left to itself under constant external conditions. If the course of the reaction is influenced from outside, then the system is an open one. Open systems are classified as follows:

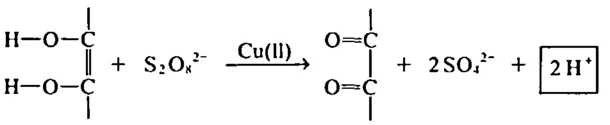
1. Flow methods
2. Steady state methods
3. "Stat" methods
4. Special variants

It is a common feature of methods 1 to 3 that a stationary condition is maintained within the system by addition of reactants or removal of products in the course of the experiment. With the flow methods and the steady state methods this condition is build up by the control of the reacting system itself, whereas with the "stat" methods it is preset from outside.

In the two former groups, kinetic data are gained by having concentrations in the stationary state, in the "stat" technique by following the process which is necessary for maintaining a particular preset condition of the system. This preset condition may be maintained by controlling the concentration of a reaction substrate or product via a measurable feature (called a command variable).

Command variables may be redox potential (potentiostat[44-46]), absorbance (absorptiostat[47]), polarization current (biamperostat[48]), chemiluminescence (luminostat[49]), and heat of reaction (thermostat[50]). The most well-known "stat" procedure, however, is the pH stat procedure, in which the protons consumed or produced in a protolytic reaction are continuously neutralized or substituted by addition of a standard acid or base, while the command variable (pH value) is potentiometrically monitored by a pH-glass electrode.

Whereas pH-stat procedures are widespread in organic chemistry and biochemistry, possibilities of application of the pH-stat methods to metal ion catalyzed reaction have been suggested only recently by Pantel.[51] Thus the copper (II)-catalyzed oxidation of ascorbic acid with peroxydisulfate proceeds according to the following equation:



$$\begin{array}{c}|\\ \text{H—O—C}\\ \|\\ \text{H—O—C}\\ |\end{array} + S_2O_8^{2-} \xrightarrow{Cu(II)} \begin{array}{c}|\\ O{=}C\\ |\\ O{=}C\\ |\end{array} + 2SO_4^{2-} + \boxed{2H^+}$$

(4)

If the reaction is carried out at pH 3.5 and 0.05 M sodium hydroxide (NaOH) is selected for keeping the preset pH constant, then the operating (dosage) speed of the autoburette (represented in dependence of mℓ NaOH → time) is a measure of catalyte concentration.

If the reaction is carried out at pH 3.5 and 0.06 M sodium hydroxide (NaOH) is selected for keeping the preset pH constant, then the operating (dosage) speed of the autoburette (represented in dependence of mℓ NaOH → time) is a measure of catalyte concentration. The following examples of pH-stat procedures were listed by Pantel:[51] determination of copper (II) (0.03 to 0.3 μg/ mℓ, 0.5 to 5 ng/ mℓ, respectively) with the indicator reaction ascorbic acid — peroxydisulfate; determination of molybdenum (VI) (0.2 to 2.5 μg/ mℓ$^{-1}$) with the indicator reaction thiosulphate — hydrogen peroxide; determination of zirkonium (IV) (0.2 to 2 μg/ mℓ$^{-1}$) with the indicator reaction iodide — hydrogen peroxide; determination of vanadium (V) (0.2 to 2μg/ mℓ$^{-1}$) with the indicator reaction iodide — bromate. In one example, the copper-ascorbic acid-peroxydisulfate reaction, it is shown that the pH-stat method has distinct advantages over closed systems, giving considerably better sensitivity for the determination of copper (0.5 to 5 ng/ mℓ$^{-1}$, special variant).

As numerous reactions, in particular redox reactions, are connected with the generation or consumption of protons, the method is a valuable contribution to catalymetry.

d. Application of Competitive Reaction Systems

The method of competitive reactions suggested by Smith and Downing[52] for the evaluation of rate constants was applied to the determination of catalyst concentration by Klockow et al.[53,54] This technique involves coupling of a relatively slow catalytic reaction with a fast competitive reaction:

$$\text{I reaction: } A + B \xrightarrow{k_1} P \quad \text{slow} \qquad (5)$$

$$\text{II reaction: } R + B \xrightarrow{k_2} P \quad \text{fast} \qquad (6)$$

with $k_2 \gg k_1$ and R = competitor.

One reactant, B, which at the same time serves as the indicator substance, is removed by the slow reaction as well as by the competitor added to the system from outside. Under suitable conditions the time for the complete removal of the indicator substance is dependent only on the rate of the catalyzed reaction and consequently on the catalyst concentration.

Two techniques have been investigated:

1. Titration with the competitor (R). R is introduced continuously into a solution containing A and B (Smith and Downing[52]) or a solution containing A, B, and a catalyst C (Klockow et al.[53,54]).
2. Titration with a reactant (B). B is introduced continuously into a solution containing A, R, and a catalyst C (Klockow et al.,[54] Müller et al.[55]).

This technique was successfully applied by Klockow et al.[54] to phosphate determination by means of the indicator reaction between molybdate and ascorbic acid:[56,57]

$$\text{Mo(VI)} + \text{acsorbic acid} \xrightarrow[k_1]{H_2PO_4^-} \text{Mo(V)} + \text{dehydroascorbic acid} \qquad (7)$$

In the presence of iodine the competitive reaction takes place:

$$I_2 + \text{ascorbic acid} \xrightarrow[k_2]{} 2\,I^- + \text{dehydroascorbic acid} \qquad (8)$$

where $k_2 \gg k_1$. Iodine is added to the system continuously at a constant rate by means of an autoburette. The time periods t_k and t_B, which are needed for free iodine to appear (t_k in the presence of the catalyst, t_B in the absence of the catalyst), are measured by potentiometric or bioamperometric sensors. A calibration graph up to 1.2 ppm phosphorus was presented. The influence of 14 accompanying ions was examined. Interference is caused by NO_2^-, S^{2-}, SO_3^{2-}, $Cr_2O_7^{2-}$ in particular.

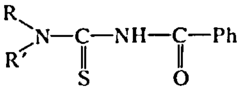
The technique described above (titration with a reactant) is also applicable to the autoinhibited[60] iodine-azide reaction, which has been thoroughly investigated:[58,59]

$$2\,NaN_3 + I_2 \xrightarrow{S^{2-}*} 3\,N_2 + 2\,NaI \qquad (9)$$

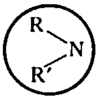
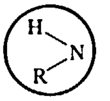
---

* Thiosulfate, metal sulfides, sulfur containing organic compounds, and metal complexes with sulfur donor atoms ligands also are acting.

Table 6
INFLUENCE OF SUBSTITUTION ON THE CATALYTIC EFFICIENCY OF *N*-BENZOYLTHIOUREAS



$$\begin{matrix}R \\ R'\end{matrix}\!\!>N-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{O}{\|}}{C}-Ph$$

	$\frac{\Delta (t_K/t_B)\cdot 10^5}{\Delta c_K}$
H_2N	65.5
Piperidine	27
$(CH_3)_2N$	21
	
p-NO_2-Ph-NH	5.1
Ph-NH	2.7
o-C_2H_5-OOC-Ph-NH	2.0
(Similar compounds)	
Thiourea	79
$S_2O_3^{2-}$	30
Cysteine.HCl	14

In this way, Müller et al.[55] determined catalytic activities of substituted *N*-benzoylthioureas in the iodine-azide reaction.

In the determination of catalytic activity of sulfur containing compounds using the azide/iodine reaction the catalyst is oxidized to an inactive form in a side reaction with iodine. Using a system of competitive reactions (reaction between ascorbic acid and iodine), in which the concentration of iodine is always kept very low during the measurement, it is possible to overcome this difficulty. In such a system sulfide is catalytically active during a considerable part of the measurement period. With this method it is possible to recognize differences in the structure dependent behavior of the investigated catalysates (*N*-benzolthioureas) and to correlate the catalytic activity with the structure.

Some results of these investigations are presented in Table 6. As a measure of the catalytic efficiency of the sulfur containing catalyst K, the quotient

$$\frac{\Delta(t_K|t_B)\cdot 10^5}{\Delta t_K}$$

was selected, where t_K = period before appearance of free iodine in the presence of the catalyst, and t_B = period before appearance of free iodine without catalyst (the only reaction is between the competitor ascorbic acid and iodine).

Table 6 clearly shows the influence of substitution on the catalytic efficiency of *N*-benzoylthioureas. Comparative investigations using the method by Kurzawa et al.[61] (iodine excess method) failed to reveal differentiation of the various catalysts into groups of varying activity. Müller and Beyer[62] investigated catalytic activity of selenium containing compounds (*N*-benzoylselenoureas) in the iodine-azide reaction using the

Table 7
OPEN SYSTEMS IN CATALYMETRY

Analyte	Comments	Ref.
Stat methods		
Mo(VI)	Potentiostat	44
Th, V, I^-	Potentiostat	45
F^-	Potentiostat	46
Catalase, Cu(II), Mo, I^- glucose-oxidase, thyroxine, 5-chloro-7-iodo-8-hydroxoquinoline, peroxidase	Biamperostat	48, 48a
I^-, Mn(II), Mo(VI)	Absorptiostat	47, 47a
Catalase, ascorbate oxidase, peroxidase, sorbitol, dehydrogenase, lactate dehydrogenase	U.V.-absorptiostat	
Cu(II), L-histidine	Luminostat	49
Cu(II), Mo(VI)	Thermo-stat	50
Cu(II), Mo(VI), Zr(IV), V(V)	pH-stat	51
Flow- and steady-state methods		
Os(VIII), I^-, Hg(II), Ag(I), L-cysteine	Steady state	216
I^-, Hg(II), Mn(II), Pb(II)	Flow-through cell	218
Ag(I), S^{2-}	Flow-through cell	226
Mo(VI)	Filter paper as medium for the reaction and the transport, monitoring with I^--sel. electrode	231
Special variants		
S^{2-}, (cysteine, phosphate)	Competitive reaction system	53
PO_4^{3-}	Competitive reaction system	54
S^{2-}	Competitive reaction system, determination of catalytic activity of sulfur-containing compounds	55
Se^{2-}	Competitive reaction system, determination of catalytic activity of selenium-containing compounds	62

method of competitive reactions in an open system and found that probably such compounds also are catalytically active.

The above examples show that catalytic methods may, under certain conditions, contribute to the solution of structural problems and may thus complete the evidence given by the usual methods of structural analysis (IR-, UV/VIS-, NMR-, EPR-, spectroscopy).

The application of open systems in catalymetry offers the following main advantages: experiments may easily be mechanized;[63] modified test conditions, adequate to the problem to be solved, are easily realized. Disadvantages are insufficient sensitivity and need of relatively large samples.

Table 7 presents a survey of the application of open systems in catalymetry.

e. Catalytic Titrations

Catalytic titrations (or catalymetric titrations) involve (1) a titration reaction, in which a catalytic titrant is added to the sample and reacts rapidly and stoichiometrically with the sought-after species, and (2) an indicator reaction, which involves the monitored species and can only occur at a noticeable rate once an excess of titrant is present in the system. Catalytic titrations are not real kinetic determinations as time is unimportant as a measured variable in these methods. The great advantage of catalytic titrations is that excess of titrant does not result in stoichiometric reaction with the indicator system, but has a catalytic effect. As catalytic effects are very sensitive, the end point is easily detectable in such titrations, the concentrations of the titrating solution may be smaller by some orders of magnitude than with classical titrations. By using catalytic titrations, 10^{-7} to 10^{-5} *M* solutions may be determined with errors of about 1%. Mottola[38] has given a very good introduction and review in the field of catalytic titrations in CRC, in 1975 ("Catalytic and Differential Rate Methods"). This article gives only a few more recent examples of the application of catalyzed indicator reactions in titrimetric analysis.

Catalytic titration methods and end-point detection were described in detail by Hadjiioannou.[64] New examples for applications of catalyzed indicator reactions in titrimetric analysis were quoted by Weisz and Pantel.[65,66] Possibilities for automated titrations with catalytic end-point indication were shown by Hadjiioannou[64] and Weisz et al.[67] Weisz[68] and Mottola[38] discussed catalytic end-point indication in volumetric analysis in correlation with other catalytic techniques. Investigations of Gaal[401] have shown the possibilities of using constant-current potentiometry and amperometry in catalytic titrations.

Hadjiioannou et al.[402] reported the determination of microgram quantities of EDTA by using a perchlorate (periodate) selective electrode. The excess of Mn catalyzes the reaction of periodate and diethylaniline. Hadjiioannou and Timotheou[403] titrated Au(III) or Pd(II) and Hadjiioannou and Piperaki[404] Hg(II) with iodide by using the Ce(IV)/As(III)-reaction.

Kreingold et al.[405] reported the determination of oxygen deficit in silica by means of catalytic titration. The acid-catalyzed acetylation reaction of alcohols and phenols with acetic anhydride was used by Greenhow[406] to indicate the end-point in the titration of tertiary amines and metal carboxylates with perchloric acid. Acids were determined by Greenhow and Nadjafi[407] by nonaqueous titrimetry and catalytic-thermometric end-point indication. Catalytic-thermometric end-point indication was also used by Kiba and Furosawa[408] for the determination of Ag(I), Hg(II), and Pd(II). The titrant was iodide and the indicator reaction the Mn(III)/As(III)-reaction. Gaal et al.[409] determined fluoride and silicofluoride with thorium nitrate as the titrant and the H_2O_2/iodide reaction as the indicator reaction. The same authors described the application of amperometric and potentiometric detection for the determination of EDTA using Cu(II) as a catalytic titrant and the decomposition of H_2O_2 as the indicator reaction.[410] Gomez et al.[411] determined amino polycarboxylic acids (EDTA, DCTA) and, indirectly, Ni(II), Hg(II), and Fe(III) by use of a new indicator reaction — oxidation of 1,4-dihydroxyphthalimide dioxime by iodate, catalyzed by Ni(II). Ternero et al.[412] reported the determination of EDTA, Mn(II), and Ni(II) with catalytic end-point indication. Pantel and Weisz[413] have given new examples for the end-point indication (biamperometry and chemiluminescence) in catalytic titrations. Weisz and Schlipf[459] described the application of gaseous catalysts for end-point indication in titrimetric analysis in the microgram range. In the titration with sodium sulfide, the first drop of titrant in excess causes evolution of hydrogen sulfide which acts as a catalyst for the indicating iodine azide reaction. The gas formed at the end-point is transferred by a nitrogen stream to the indicator vessel. Metal ions (Sb, Ni, Fe, Hg + Cd, Pb + Cu, Ag + Cu) and permanganate can be determined. Amperometry and constant-current potentiometry were used to follow the course of catalytic titrations of silver(I), palladium(II), and mercury(II) with potassium iodide. The Ce(IV)/As(III) and Ce(IV)/Sb(III) systems in the presence of sulfuric acid were used as the indicator reactions.[414] Gaal et al.[415] reported the catalytic titration of DCTA with Co(II) and Mn(II) and amperometric, potentiometric and spectrophotometric end-point determination. Pantel and Weisz[397] demonstrated the application of catalytic end-point indication to redoxtitrations. A catalytic titration for rapid determination of small amounts of iodine in phosphorus ores was described by Cheng et al.[416]

Table 8
RANGE OF APPLICATIONS OF KINETIC METHODS OF INVESTIGATION METHOD

	$t_{1/2}$ (s)
Conventional methods	$\sim 10^{1}$—10^{4}
Flow methods	$\sim 10^{-3}$—10^{1}
NMR	$\sim 10^{-5}$—10^{0}
Electrochemical methods	$\sim 10^{-6}$—10^{0}
Flash photolysis	$\sim 10^{-7}$—10^{0}
EPR	$\sim 10^{-9}$—10^{-4}
Relaxation methods	$\sim 10^{-9}$—10^{-1}

Despite obvious advantages and uses illustrated above, catalytic titrations have not been widely used in routine analysis so far.

3. Monitoring Reaction Rates

If the stoichiometry and quantitative characteristics are known (irreversible and without side reactions), it is sufficient to observe consumption or formation of a substance participating in the reaction (indicator substance). Variation of concentration of the indicator substance with time may be observed using chemical, electrochemical, or physical methods. If chemical methods are applied, frequently sampling of the reacting solution and analysis is necessary. In this case, the determination of the concentration should be fast relative to the reaction going on, otherwise the reaction must be interrupted by cooling, diluting, removal of one reacting partner or of the catalyst. This technique is only applicable in a few cases of catalytic determinations (e.g., in determining sulfide by means of the iodine-azide reaction,[61,69] in determining Fe(III) by catalytic decomposition of H_2O_2,[70] in determining iodide according to the Sandell-Kolthoff reaction[71]).

Electrochemical principles of analysis are based on studies of reactions at electrodes and processes between them, respectively. As regards the way of obtaining information we can distinguish two methods: methods of determination in which direct analytical information is obtained from electrical process variables, and methods in which electrical variables are used for end-point indication in catalytical titrations. Both types are applied in catalymetry.

Selection among very accurate and sensitive methods (amperometry) or universally applicable methods (potentiometry) is possible and also the application of coulometric generation of reagents may be applied. Methods of analysis based on physical effects are fast and may be rather easily automated, and they do not interfere with the reacting system. Any physical property is suitable for measurement if it undergoes sufficient change in the course of reaction. The application of physical methods of measurement raises new possibilities for using fast and very fast reactions in kinetic analysis. This opens the way for the practical application of indicator reactions with very small half-times (<10 s) in catalymetry. Table 8 shows the range of applications of various kinetic methods of investigation (according to Schwetlick[72]).

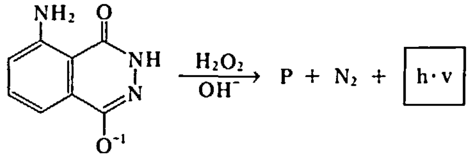
If the concentration of a substance participating in a reaction is measured using a variable which is proportional to the quantity to be determined, then in most cases the corresponding functional equation represents a simple linear relation $y = p \cdot x$, where y = variable proportional to concentration, p = proportionality factor, and x = concentration.

The sensitivity of the method of investigation and thus of the process of catalytic determination depends significantly on the quantity of the factor p (and thus on the type of indication selected; dy/dx should be as large as possible). The example of the sulfide-catalyzed iodine-azide reaction makes this obvious.

Measurement of the increase of nitrogen volume (N_2 as indicator substance) enables determination of microgram quantities of the catalyst.[73] The more sensitive photometric method based on measuring the decrease of iodine concentration (I_2 as indicator substance) shifts the limit of determination to the nanogram range.[74] Application of an amperometric technique of following the indicator reaction results in the determination of sulfides in the picogram range.[75]

For determination of concentration in solution, spectrophotometry, because of its wide application, holds a special position. Catalytic-spectrophotometric determinations are, therefore, of great significance.

Measurements of fluorescence are gaining more and more significance for kinetic-catalytic processes. Photoelectric fluorescence (luminescence) methods are highly sensitive, but they require particular measuring techniques because of the special features of fluorescent radiation. This measuring technique is important for indication of metal-catalyzed chemiluminescence reactions. The metal-catalyzed oxidation of some organic compounds, e.g., lucigenin, luminol, and amidol by H_2O_2 is accompanied by light emission.[76-78]



The amount of radiation emitted per unit time is proportional to the catalyst concentration and can be measured by the blackening of a photographic plate or by a photomultiplier.[79] Recently, application of thermometric (enthalpimetric) methods has increased. Although this is the most unspecific indication method, as every reaction is accompanied by a conversion of energy, the application of thermistors opens new possibilities, as minimal temperature changes are exactly measurable with simple technical means. However, at present this type of indication is more or less limited to catalytic titrations with thermometric end-point indication (a catalyzed reaction connected with a great amount of heat evolved at the equivalence point), since exact enthalpimetric measurements of the course for the reaction are based on thermal equilibrium (consideration of heat of mixing and dilution, which, however, is not realized in a kinetic way) and are, therefore, very time-consuming.

a. Application of Ion-Selective Electrodes[80-82]

The application of potentiometric methods for following changes in the concentration of an indicator substance has increased recently.

Potentiometry is the currentless measurement of cell voltages in equilibrium for determining activities (concentrations) of solution species. The basis of potentiometric measurements is the Nernst equation, which, after application of the usual simplifications, takes the following form:

$$E_{eq} = E' \pm \frac{2.3\ RT}{z_i \cdot F} \ell g\ a_i \qquad (11)$$

where E_{eq} = potential of the indicator electrode, E' = portion of the total potential due to choice of reference electrodes and internal solution, and R and F are the ideal gas and Faraday constants, respectively. T is the absolute temperature; z_i = number of exchanged electrons per molecule in the electrochemical reaction.

As is well-known, 2.3 RT/F has the theoretical value of 59.2 mV for $z_i = 1$ and $T = 298$ K. With these values a tenfold change of a_i (c_i) results in a potential difference of $\Delta E = 59$ mV. Therefore, in direct potentiometric measurements slight variations in the measurement of E_{eq} result in considerable errors. A variation of $\Delta E = 1$ mV results in a error of 4%, when single-charged ions are determined.[80,83] From this it may be deduced that this type of indication cannot compete with most other methods with respect to sensitivity. Thus, the application of potentiometry for catalymetry is recommended only when measurement of the reaction with photometry fails or the latter is less sensitive.

Ion-selective electrodes are mainly used in catalymetry for

1. Catalyzed reactions with I^- as reducing agent

$$2\,I^- + ox \xrightarrow{K} I_2 + red \qquad (12)$$

and measurement of $-[I^-]/dt$
2. Reactions of halates (XO_z^-) as oxidizing agent in reaction with various agents

$$XO_z^- + red \xrightarrow{K} X^- + ox \qquad (13)$$

via measurement of $[X^-]/dt$ or direct measurement
3. $-[XO_z^-]/dt$, respectively, using halide- or halate-sensitive electrodes (Table 9 shows applications of ion-selective electrodes in catalymetry.)

Catalytic techniques are very sensitive.[38,63] If a modification of technique operation with minimal sample and reagent volumes becomes possible (micro- and ultramicro-techniques[84,85]), extreme trace analysis in micro-objects can be carried out. For certain tasks of geology (extraterrestial materials), pollution control analysis (determination of essential or toxic constituents), forensic analysis, and biology (intracellular measurements), this modification is an urgent requirement. The latter possibility was pointed out by Yatsimirskii as early as 1973: "The possibility of detecting individual molecules with the help of catalytic reactions becomes apparent if we take into account the use of ultramicroanalytical techniques such as spectrophotometric measurements in very small volumes."[37]

Although micro- and ultramicro-variants have been worked out for photometric techniques in particular,[86] the combination of ultramicro-techniques and catalymetry has not been achieved yet. The application of techniques of catalytic-potentiometric determination on a micro- or ultramicro-scale seems experimentally rather simple.

Based on the reaction between H_2O_2 and iodide

$$H_2O_2 + 2\,I^- \xrightarrow{Mo(VI)} I_2 + 2\,H_2O \qquad (14)$$

a method for the determination of molybdenum on a micro-scale (total volume 100 μℓ) which is capable of determining 2 ng of molybdenum was worked out by Müller et al.[87] A screw-in electrode based on a solid membrane (Ag_2S/AgI) is used as the working electrode. The reference electrode is a solid membrane electrode as well, based on $Ag_2S/AgBr$ (see Figure 4).

Table 9
SOME APPLICATIONS OF ION-SELECTIVE ELECTRODES IN THE CATALYMETRY

Reaction	Electrode	Comments	Ref.
$I^- + H_2O_2$	I^--selective	Study of the uncatalyzed reaction	398
$I^- + H_2O_2$	I^--selective	Determination of Mo and W	399
IO_4^- + amino alcohol	ClO_4^--selective	Determination of Mn	334
$IO_4^- + AsO_3^{3-}$	IO_4^--selective (ClO_4^--selective	Determination of Cr	291
Perbromate + I^- (Fe-induced)	I^--selective	Determination of Fe, BrO_4^-, EDTA, DTPA	268
Chloramine T + H_2O_2	Chloramine T-selective	Microdetermination of I^-	283
Chloramine T + As(III)	Chloramine T-selective	Determination of I^- and Os(VIII)	252
I^- + peroxoborate	I^--selective	Determination of Mo(VI)	251
I^- + peroxoborate	I^--selective	Determination of W and V	243
BrO_4^- + tartaric acid (Fe-induced)	BrO_4^--selective	Determination of tartaric acid	234
$I^- + H_2O_2$	I^--selective	Determination of Mo, ultramicrotechnique	87
$I^- + H_2O_2$	I^--selective	Determination of Mo, flow method	231
$CH_3\text{-}\underset{\underset{O}{\Vert}}{C}\text{-}CH_3 + I_2$	I^--selective	Determination of I^-, $1\text{—}5 \times 10^{-5}$ *M*	232

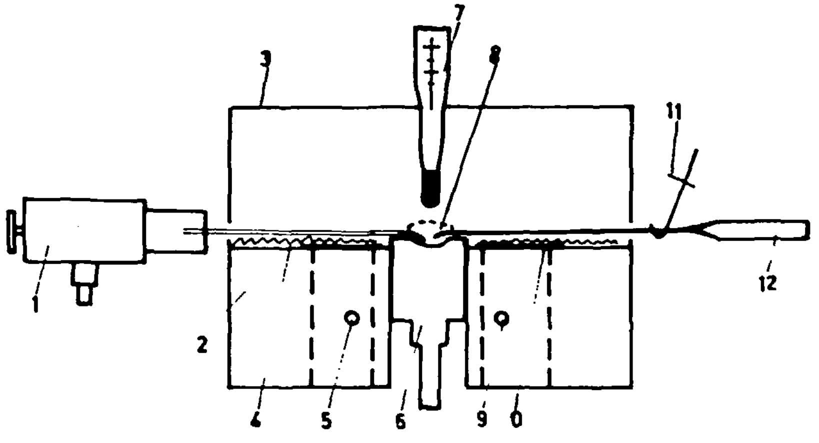


FIGURE 4. Measuring equipment for work with ion-selective electrodes in the micro-range. (1) $Ag_2S/AgBr$ reference electrode; (2) moist chamber; (3) removable cap; (4) moist cotton batting; (5, 9) connection for thermostat; (6) I^--selective electrode (Ag_2S/AgI base); (7) thermometer; (8) measuring solution; (10) brass plate; (11, 12) vibrator.

Figure 4 shows the working chamber which is kept moist. The apparatus is completed by a thermostat and a pH-test amplifier with digital display (resolution 0.1 mV). Measurement is evaluated using the integrated velocity equation, assuming reactions of the pseudo-first order with reference to iodide as the reducing agent according to a modified variant of the method of tangents.

4. *Types of Catalytic Reactions Used in Analytical Procedures*

Catalyzed reactions may have different mechanisms. Knowing these is far more important with kinetic-catalytic methods than with methods based on chemical equilibrium. In the latter procedures proportionality between concentration of the substance to be determined and one parameter of the reaction in equilibrium is sufficient for analytical purposes, no matter at which stage of reaction the equilibrium is attained. The more knowledge is obtained on the mechanism of a catalytic reaction, the more easily one will find the most favorable conditions for analytical application of the reaction as regards sensitivity, accuracy, and selectivity.

On the basis of reaction mechanisms, indicator reactions may be classified as follows:[37,38]

I. Metal-catalyzed reactions
  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. Double ligand exchange
  C. Reactions with carbonyl compounds
    1. Hydrolysis reactions
    2. Decarboxylation reactions
  D. Reactions using enzymes
    1. Activation effect
    2. Inhibition effect
II. Reactions for the determination of nonmetallic species
  A. Primary catalytic effects
    1. Redox reactions
    2. Reactions with carbonyl compounds
    3. Reactions with coordination compounds
  B. Secondary effects
    1. Activation effect
    2. Inhibition effect

Since applications of various reaction types in catalymetry has been reported elsewhere,[36,38,63] the intention here is to mention only a few special and recent applications.

a. Catalyzed Redox Reactions and their Application for Determination of Platinum Metals

The most sensitive catalytic metal determinations are based on catalyzed redox reactions. Metal concentrations from to 10^{-9} to 10^{-7} g mℓ^{-1} may be determined, in special cases (Os, Ru) to 10^{-12} g mℓ^{-1}.

Redox reactions are associated with a change of the state of oxidation of the reacting partners, either by electron exchange or by atom (molecule) transfer.[88,89]

In aqueous solutions atom or group transfer prevails over electron transfer. For assessment of the position of equilibrium and thus predictions of the course of redox reactions on a thermodynamic basis, the standard potentials of the participating redox pairs may be used.

Thermodynamically, a redox reaction

$$Ox_1 + Red_2 \rightleftharpoons Red_1 + Ox_2 \qquad (15)$$

is possible, if the standard electrode potential is

$$U_H^0\,(Ox_1/Red_1) > U_H^0\,(Ox_2/Red_2) \qquad (16)$$

As an indicator reaction, a redox reaction is only possible, if it is kinetically inhibited (inhibition of the orbital overlapping of the occupied orbitals of the oxidizing agent with the unoccupied ones of the reducing agent in electron transfer reactions or the necessity of fission of a covalent bond with atom or group transfer).

For the redox-catalytic effect of a metal ion on an indicator reaction associated with valency change of the catalyst, the following steps may be outlined:

$$Red_1 + M^{(n+1)+} \longrightarrow Ox_1 + M^{n+} \qquad (17)$$

$$Ox_2 + M^{n+} \longrightarrow Red_2 + M^{(n+1)+} \qquad (18)$$

The real potential of the catalist redox pair should be intermediate between the potentials of the reactants, i.e.

$$U_H\,(Ox_1/Red_1) > U_H(M^{(n+1)+}/M^{+}) > U_H\,(Ox_2/Red_2) \qquad (19)$$

Transition metals, which are the most effective catalysts in redox indicator reactions, meet the above requirements best. Catalyzed redox reactions are of great significance in the determination of platinum metals.

In nature, platinum metals mostly occur together. Their proportion in the earth's crust is between 10^{-8} and $10^{-6}\%$. The low concentrations of platinum metals and their erratic occurrence, e.g., in minerals and alloys, make quantitative analysis of these elements difficult. On the other hand, application of the platinum metals in technology is increasing, which requires the development of analytical methods for determining trace concentrations of these elements in various metals.

For quantitative determination of platinum metals both chemical (gravimetry, volumetry, spectrophotometry) and spectroscopic (AES, AAS, MS) techniques are employed. Frequently, however, sensitivity is not adequate for trace analytical determinations or may only be achieved after technically complicated concentration and separation procedures. Apart from radiochemical techniques, techniques of catalytic analysis have proved useful for the determination of platinum metals. The high power of detection of these techniques permits determination of contents down to $10^{-8}\%$ with satisfactory reproducibility and, in some cases, surprising selectivity. The special importance of redox reactions for the determination of platinum metals can be explained by the electronic configuration of these elements and the related chemical properties. This results in the following distinctive features: (1) favorable position of the potentials of the important redox pairs of these elements (see Table 10); (2) The oxidation states change in one-electron steps; and (3) great number of vacant d-orbitals. These favorable presuppositions for catalytic effects in redox processes are best realized in the case of Os, Ru, and Ir, less well with other platinum metals Rh, Pd, and Pt, in which redox reactions usually proceed in two-electron steps ($Rh^{I/III}$, $Pd^{II/IV}$, $Pt^{II/IV}$) which are connected with the transfer of atoms. This explains why only a few homogeneously catalyzed redox reactions are known for Rh, Pd, and Pt, whereas Os, Ru, and to a certain extent Ir exhibit a catalytic effect in a variety of redox reactions. A selection of normal redox potentials of oxidants, reductants, and catalysts (platinum metals) is presented in Table 10.

Difficulties in working out techniques of catalytic determinations for platinum metals

Table 10
NORMAL REDOX POTENTIALS OF OXIDANTS, REDUCTANTS, AND CATALYSTS

Redox Systems

Oxidants	Normal potential, V
Oxidants	
$Ce(IV) + e \rightleftharpoons Ce(III)$	1.44—1.7
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$	1.5
$IO_4^- + 2H^+ + 2e \rightleftharpoons IO_3^- + H_2O$	1.8
$BrO_3^- + 6H^+ + 6e \rightleftharpoons Br^- + 3H_2O$	1.44
$ClO_3^- + 6H^+ + 6e \rightleftharpoons Cl^- + 3H_2O$	1.45
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	1.77
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	1.0
Reductants	
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	0.91
$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons HAsO_2 + 2H_2O$	0.56
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	1.36
$I_2 + 2e \rightleftharpoons 2I^-$	0.53
$Tl^{3+} + 2e \rightleftharpoons Tl^+$	1.28
Catalysts	
$OsO_4 + 4H^+ + 4e \rightleftharpoons OsO_2 + 2H_2O$	0.96
$RuCl_5OH^{2-} + H^+ + e \rightleftharpoons RuCl_6^{2-} + H_2O$	1.3
$IrCl_6^{2-} + e \rightleftharpoons IrCl_6^{3-}$	1.02
$RhCl_6^{2-} + e \rightleftharpoons RhCl_6^{3-}$	1.2
$RhO_2 + 4H^+ + 6Cl^- + e \rightleftharpoons RhCl_6^{3-} + 2H_2O$	1.4

arise from: complicated and complex sequestering behavior of these metals; slowness to attain complex equilibrium; formation of polynuclear complexes.

It is essential for the catalytic ability of the catalyst that it reacts with the reactant with formation of an intermediate complex (see Yatsimirskii[89,90]). A decisive role is therefore played by the coordination sphere of the ion acting as catalyst, particularly with the kinetically inert complexes of platinum metals.[88,90]

Chloro-complexes of platinum metals frequently exhibit less catalytic activity, whereas substitution of Cl^- by H_2O, alcohols, OH^-, or SO_2^{2-} provides higher catalytic activity. This is exemplified by Figure 5, showing the varying effect of Ruchloro-complexes and Ru-sulfato-complexes on the redox reaction between Mn(III) and p-benzoquinone (Müller et al.[91]).

For analytical practice it may be concluded that the platinum metal to be determined must be involved in the catalytic reaction with a defined coordination sphere, which must frequently be enforced by drastic conditions (e.g., evaporation of the sample with a concentrated acid). Neglecting this results in erroneous and hardly reproducible data of catalytic determinations. As oxidizing agents in indicator reactions for the determination of platinum metals, most frequently cationic agents such as Ce(IV), Mn(III), Fe(III) are used as well as halates and H_2O_2. As reducing agents, Hg(I), Sn(II), and As(III) and various aromatic amines are common.

Reviews of the field of catalytic determinations of platinum metals were given by Orlova and Yatsimirskii,[90,93] of catalytic determinations of Ru and Os by Shlenskaya et al.[94] A selection of the most sensitive and selective procedures of catalytic determination for platinum metals is presented in Table 11.

i. Application of Heterogeneously Catalyzed Reactions

In general, considerations of the application of catalytic techniques in quantitative

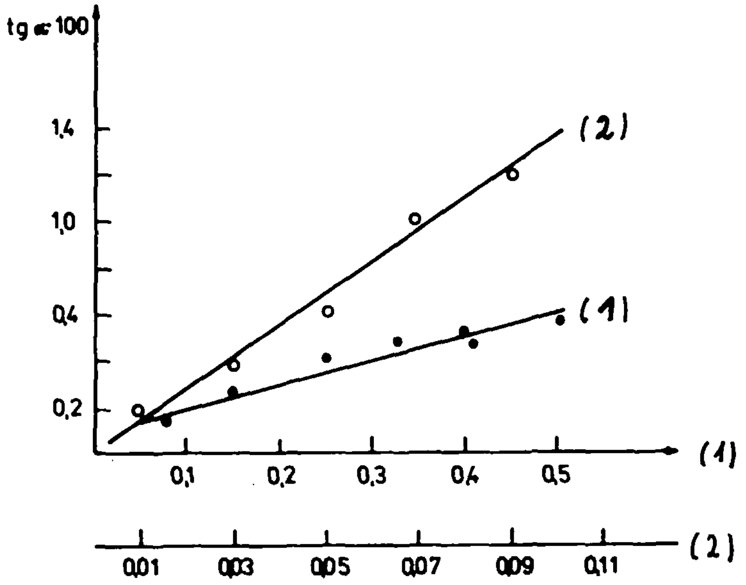


FIGURE 5. Effect of Ru-chloro-complexes (1) and Ru-sulfato-complexes (2) on the redox reaction between Mn(III) and *p*-benzoquinone.

Table 11
CATALYTIC METHODS FOR THE DETERMINATION OF PLATINUM METALS

K	Indicator reaction	Limit of detection (μg/mℓ)	Interference by platinum metals
Os	Ce(IV) + As(III)	2×10^{-5}	Ru
	$BrO_3^- + I^-$	4×10^{-5}	Ru
Ru	Ce(IV) + As(III)	2×10^{-5}	Os
	Mn(III) + p-anisidine	10^{-3}	—
	Mn(III) + p-benzoquinone	5×10^{-3}	$PdCl_2$
Ir	Ce(IV) + Hg(I)	10^{-3}	Ru
	IO_4 + o-anisidine	10^{-5}	Ru, Pd
Pd	Cl^- + Mn(III)	4×10^{-3}	—
	Ce(IV) + Hg(I)	10^{-3}	Ir, Ru
	IO_4^- + o-anisidine	10^{-1}	Ir, Ru
Pt	Fe(III) + $SnCl_4^{2-}$	3×10^{-3}	Os, Ru, Pd, Ir, Rh
Rh	$Mn^{2+} + BrO^-$	10^{-4}	Ir

analysis include only homogeneously catalyzed reactions. It was, however, suggested in the 1960s to also employ heterogenous reactions for quantitative catalytic determinations. It has sometimes been pointed out that enzymatic reactions, too, should be considered as "microheterogeneous" reactions.

However, in the redox-catalytic determination of platinum metals genuine heterogeneous catalysis is observed. Heterogeneous reactions means in this context that one reacting partner (reactant or catalyst) occurs in the reaction as the solid phase, often invisible macroscopically.

Chloride compounds of palladium and colloidal solutions of palladium and iridium catalyze the reduction of silver ions by bivalent iron.[95] The catalytic effect of Pd and Ir is explained by the formation of active centers of crystallization of silver on metallic Pd- and Ir-particles (with palladium chloride this is preceded by a reduction to metallic Pd).

The reaction may be traced spectrophotometrically or nephelometrically by measuring the amount of silver formed. Down to 2×10^{-6} μg Pd/mL and 1.5×10^{-5} μg Ir/mL, respectively, are said to be determinable with relative errors of approximately 10%.[93] This means that these would be the most sensitive techniques of catalytic determination. Gold, as well, may be determined with great sensitivity by this reaction.

Oxidation of Sn(II) by arsenite is catalyzed by Pd(II):[96]

$$SnCl_4^{2-} + HAsO_2 + 6\,H^+ + 6\,Cl^- \xrightarrow{Pd(II)} 3\,SnCl_4 + 2\,As\downarrow^\circ + 4H_2O \qquad (20)$$

The course of the reaction is controlled through the colloidal arsenic formed. Down to 0.2 μg Pd/mL may be determined with an error of approximately 10%.

Pd(II) and Rh(III) in the form of their chloro-complexes catalyze the reduction of silver in photo-emulsions by hydroquinone.[97] From the amount of liberated silver the reduction rate may be evaluated, and 1 μg Pd/mL and 0.05 μg Rh/mL, respectively, may be determined.

A very sensitive method for the determination of Rh(III) and Ir(IV) is based on the catalytic effect in the reaction of Mn(II) and hypobromite in slightly alkaline solutions:[98,99]

$$2\,Mn^{2+} + 5\,BrO^- + 6\,OH^- \xrightarrow{Rh(III),Ir(IV)} 2\,MnO_4^- + 5\,Br^- + 3\,H_2O \qquad (21)$$

The reaction proceeds via MnO_2. The authors explain the complicated mechanism of catalysis by the formation of an active complex compound between the catalyst (Rh or Ir) and the oxidizing agent hybobromite and subsequent interaction of this complex in the form of a surface reaction with MnO_2 with formation of permanganate (simultaneously indicator substance). By this method down to 10^{-4} μg Rh/mL and 10^{-5} μg Ir/mL may be determined.

An analytical application of heterogenous catalysis was described by Dutt and Mottola[209] for the determination of palladium (II), which was found to significantly increase the rate of reduction of organic dyes by hypophosphite after a brief induction period. In the final step of the catalytic process, hypophosphite reduces Pd(II) to Pd(O). In contact with finely divided metallic palladium, hypophosphite decomposes producing hydrogen which reduces the dye. The length of the induction period is inversely proportional to the palladium concentration.

ii. Application of Oscillation Reactions

For the catalytic determination of metal ions oscillating reactions may be applied. In well-stirred systems such reactions exhibit periodical change of concentration of the reactants. The first report on an oscillating chemical reaction appeared in print in 1928. Fechner[100] described an electrochemical cell which produced an oscillation current. In 1896 Liesegang[101] discovered the periodic precipitation patterns (Liesegang phenomenon). Oscillations in closed homogeneous systems were considered as impossible. The first important publication on homogeneous chemical oscillations was a theoretical paper by Lotka,[102] which appeared in 1910.

Bray[103] discovered in 1920 that the reaction mixture composed of hydrogen peroxide

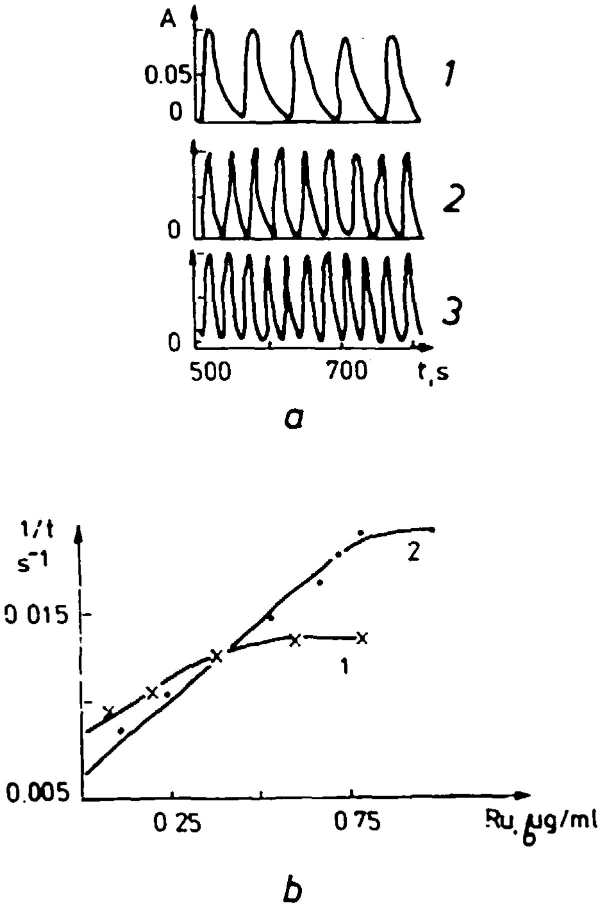


FIGURE 6. (a) Influence of Ru(III/IV) on the oscillating process in the bromate-cerium-malonic acid system: (1) in absence of the catalyst; (2) 3×10^{-6} *M* Ru(III, IV); (3) 1×10^{-5} *M* Ru(III, IV). (b) Dependence 1/t on Ru concentration: (1) Mn(III) as oxidizing agent; (2) Ce(IV) as oxidizing agent.

and potassium iodate in dilute sulfuric acid can produce an oscillation in the concentration of free iodine and in the rate of oxygen evolution.

The second case of oscillation in a closed homogeneous system was discovered in 1958 by Belousov.[104] He mixed potassium bromate, ceric sulfate, and citric acid in dilute sulfuric acid and found that the ratio of concentrations of the Ce(IV) and the Ce(III) was oscillating. Zhabotinskii[105] has studied this reaction intensively and substituted citric acid by other carboxylic acids. Most studies on this reaction have been done with cerium and malonic acid. The oscillation can be made easily visible by use of a redox indicator such as ferroin (Belousov-Zhabotinskii-reaction). This reaction was further studied by Degn,[106] Kasperek and Bruice,[107] Neyes,[108] et al., and has been used as a demonstration for a reaction periodic in time and space by Field,[109] Lefelhocz,[110] Demas, and Diemente.[111]

The catalytic effect of the primary catalyst cerium is, however, too weak to permit trace analytical determinations. Yatsimirskii[112,113] examined the influence of other ions and compounds. It was also found that the primary catalyst cerium (IV) may be replaced by Mn(III). Alcohols reduce the amplitude of oscillation and increase their frequency. Acetone and formaldehyde behave in a similar way.[114] Of analytical interest is the influence of "secondary" catalysts on oscillation. Ru(III/IV) compounds increase the frequency of oscillation and are therefore determinable in the nanogram range. For indication photometric and potentiometric techniques were applied.[113] Figure 6 a shows the influence of Ru(III/IV) compounds on the course of an oscillating reaction; Figure 6 b shows the dependence of the oscillation frequency on the concentration of the "secondary" catalyst (Yatsimirskii et al.[113]).

The authors try to give a mechanistic explanation of the catalytic effect of ruthenium compounds, based on the general pattern of the course of the Belousov-Zhabotinskii-reaction (e.g., according to Degn[106]).

Oscillating reactions are not only interesting from the aspect of analysis, but they also provide insight into cyclic, oscillating systems in nature in general (such as the heart beating, the lungs pumping, the cancer cycle, or any of the many so-called biological "clocks"), and they are excellent objects for demonstrating the effects of various parameters (temperature, concentration of reactants and catalysts and others) on the course of a catalytic reaction.[109,111]

b. Determination of Nonmetallic Species

i. Primary Catalytic Effect[38,63]

The main field of application of catalytic techniques has so far been the determination of metal traces, as may be seen from Figure 10. There are only a few nonmetals which are determinable by primary catalytic effects.

Due to the rapid development of techniques of atomic spectroscopy (AAS, AES with new sources of excitation such as ICP, MIP, and others) and electrochemical methods (e.g., differential pulse polarography), determination of metal traces with high sensitivity, good selectivity, and accuracy, even as a multielement procedure, is rather easy (although sophisticated technical equipment is necessary). Therefore, the development of new catalytic methods for the determination of metal traces is justified only in such cases where for certain reasons, the power of detection of existing techniques is insufficient (e.g., not easily vaporizable or carbide-forming elements in flameless AAS; polarographically inactive elements in pulse polarography), or where the examination of chemical individuality (oxidation state examination considerations of the degree and/or state of complex formation) of a metal ion demands a chemical technique. The development of new catalytic methods of determination for nonmetallic species will therefore gain more and more importance, either as a supplementary or as a comparative technique for HPLC and ion chromatography. Since only a few catalytic effects for the determination of nonmetallic species are known, indirect techniques of determination must be employed.

ii. Indirect Techniques

The complex-forming ability of anions and organic compounds, which is often rather marked, permits determination of these species (ligands) due to their influence on metal-ion-catalyzed indicator reactions.

In the interaction of ligands (L) with metal ions having a catalytic effect

$$M + L \rightleftharpoons ML \qquad (22)$$

the following correlations may be found (cf. Janjic et al.,[132] Mottola,[133] and Guilbault[134]):

1. The complex compound ML is catalytically inactive (complete inhibition). With a stoichiometric (equimolar) ratio of metal and ligand the reaction rate is zero (Figure 7, line a).

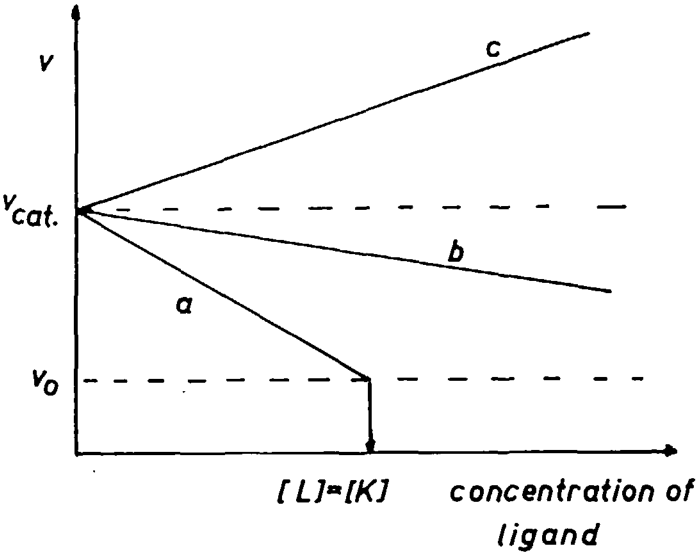


FIGURE 7. Influence of ligands on a metal-catalyzed reaction (diagrammatic representation). L = Ligand; K = catalyst; v_0 = reaction rate of the blank reaction; v_{cat} = reaction rate of the catalyzed reaction; a, b, c = see text.

2. The complex compound ML is catalytically less active than the noncomplexed metal ion (partial inhibition), and the complex formation constant (K_{ML}) has a small value (Figure 7, line b).
3. As catalyst the complex ML is more active than the metal ion alone, and the reaction rate increases (Figure 7, line c).

Inhibiting effects may be widely applied for the determination of nonmetallic (complex-forming) species. Some examples of the application of metal-catalyzed redox reactions for the determination of nonmetallic species are given by Dolmanova et al.,[136,336] and Antonov and Kreingold.[135]

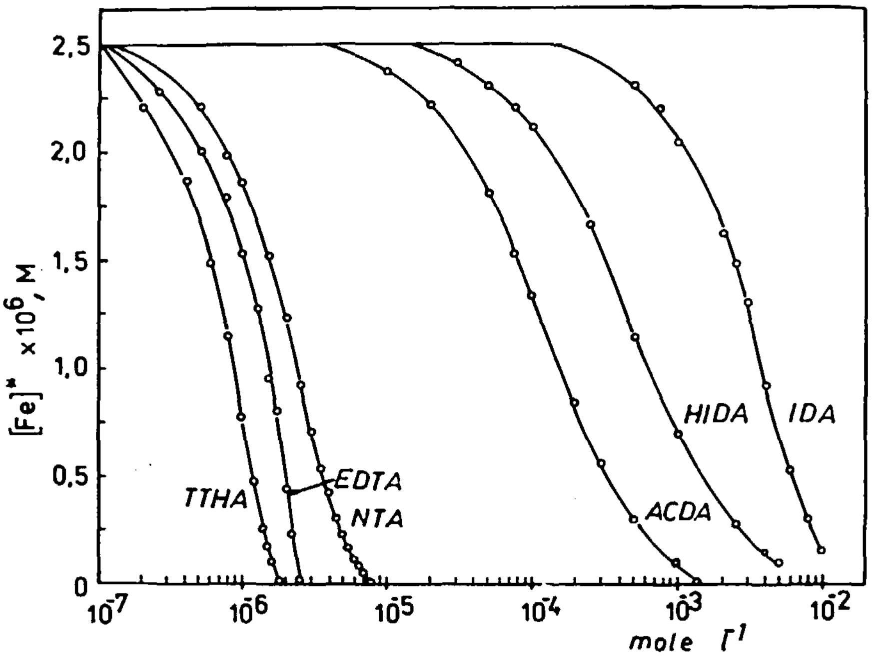
The relations between the stability of the complex compound ML and the inhibiting effect, illustrated in Figure 7 are obvious in the example of the Fe-catalyzed reaction between p-phenetidine and H_2O_2 with 1,10-phenanthroline as the activator, inhibited by α-aminopolycarboxylic acids and phosphates. This reaction was examined by Müller et al.[137]

The application of this indicator reaction for indirect kinetic-catalytic determination of α-aminopolycarboxylic acids and phosphates is thought to be adequate for the following reasons:

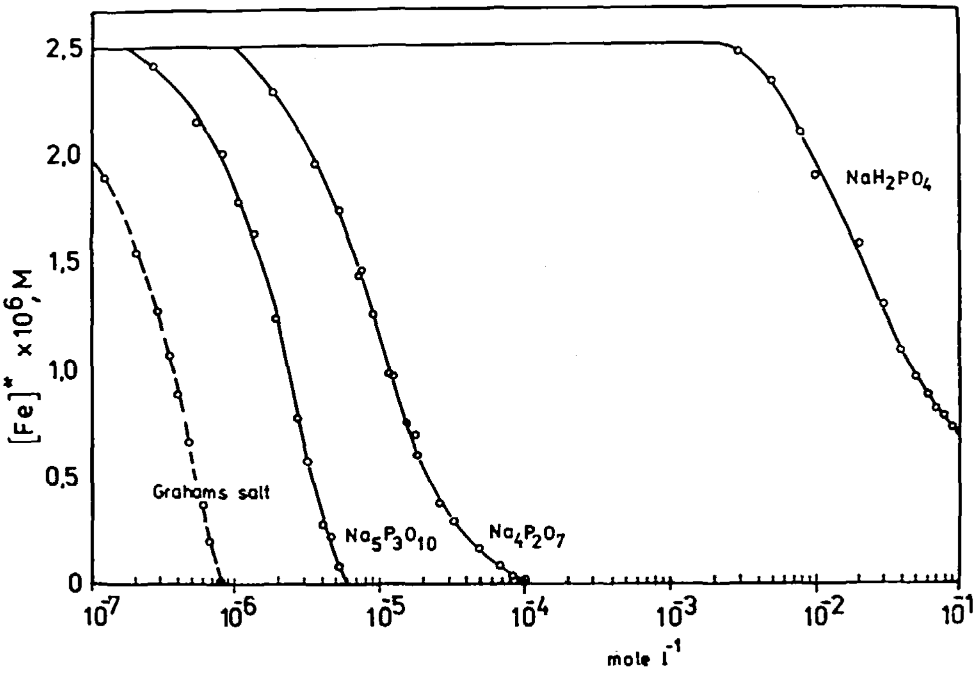
1. Fe(III) forms very stable complexes with α-aminopolycarboxylic acids and phosphates.
2. The indicator reaction is very sensitive towards the iron catalyst and thus very sensitive techniques of determination of the ligands may be expected.
3. The activator 1,10-phenanthroline, by competitive reaction with the catalyst iron, may differentiate the inhibiting action of the various ligands.

A mechanistic interpretation of the Fe-catalyzed reaction between p-phenetidine and H_2O_2 is given by Bontchev[138] and for the inhibited reaction by Müller et al.[137]

If the stability of the catalyst-inhibitor complex (ML) is very large, the reaction will be



A



B

FIGURE 8. Inhibitor behavior of α-aminopolycarboxylic acids (a) and phosphates (b) on the Fe-catalyzed oxidation of *p*-phenetidine by H_2O_2. TTHA = triethylenetetraminehexaacetic acid; EDTA = ethylenediaminetetraacetic acid; NTA = nitriloacetic acid; ACDA = 2-aminocyclohexanole-N,*N*-diacetic acid; HIDA = *N*-hydroxyethyleneiminodiacetic acid; IDA = iminodiacetic acid.

completely stopped by ligand amounts equimolar to the catalyst (Figure 7, line a). With suitably high amounts of inhibitor, even less "strong" ligands may result in halting of the reaction (Figure 7, line b). Considering all interactions of the catalyst with the potential ligands in the reacting solution (1,10-phenanthroline, chloride ions, water, p-phenetidine, reaction products, H_2O_2), it was found[137] that with a conditional stability constant K_{ML} of $\sim 2 \times 10^{10}$ the reaction is stopped already at equimolar ratios of the ligand and metal (tetra-, penta-, and hexa-acids). Di- and tri-acids as well as phosphates cause inhibition of the catalytic effect of iron only if added in great excess (Figure 8, a and b). The reaction described is suitable for quantitative determination of tri- to hexa-aminocarboxylic acids in a concentration range from 2.5×10^{-7} to 2.5×10^{-6} *M* with good reproducibility.

The application of activators for improving detection limits in catalymetry (Bontchev[154]) generally includes the possibility of quantitative determination of the substances used as activators. However, only a few examples of practical application have been reported:

- Nitrilotriacetate (NTA) activates the Mn (II)-catalyzed reaction between malachite green and periodate and may thus be quantitatively determined.[139]
- Metal-catalyzed reactions between luminol and H_2O_2 are activated by ligands.

NTA may be determined within the 10^{-7} to 10^{-6} mol l^{-1} range, the ligands 1,10-phenanthroline, 2,2-dipyridyl, ethylendiamine, histamine, 8-hydroxyquinoline in the nanogram range.[140]

Ascorbic acid has an activation effect on the V-catalyzed iodide chlorate-reaction. It depolymerizes polyvanadate and may, due to this effect, be determined down to 0.5 μg/mℓ.[141]

C. Sensitivity and Selectivity of Catalytic Methods

1. Sensitivity

a. Power of Detection

Catalytic analytical methods are characterized by the low limit of detection and high sensitivity. These features characterize trace analytical procedures in general. Their exact values depend on the practical conditions of analysis and may be accurately determined by statistical calculations.

One principle of analysis[142] is characterized by the term "power of detection" introduced by Kaiser and Specker.[143,144] It is an estimated value for the power of detection of an idealized analytical method in which external interfering factors are more or less neglected.

For catalytic determination based on the equation

$$A + B \xrightarrow{K} X + Y \tag{23}$$

under the conditions of initial rate with X as the indicator substance and of neglection of the noncatalytic reaction, we get

$$v_i = \frac{\Delta[X]}{\Delta t} = k_k[K]\Pi_c \tag{24}$$

where $\Pi_c = [A]_0\,[B]_0$; k_k = rate constant of the catalyzed reaction.

In order to assess the power of detection of catalytic spectrophotometric technique it is necessary to start from the Lambert Beer Law, which has the following form when the absorbance of the indicator substance X is measured:

$$\Delta A \cdot \epsilon_\lambda \cdot d \cdot \Delta[X] \tag{25}$$

If Equation 24 is adjusted for $[K]_{min}$

$$[K]_{min} = \frac{\Delta[X]_{min}}{\Delta t_{max} \cdot \Pi_{c_{max}} \cdot k_{k_{max}}} \tag{26}$$

and this expression is inserted in Equation 25, it follows that

$$[K]_{min} = \frac{\Delta A_{min}}{\Delta t_{max} \cdot \Pi_{c_{max}} \cdot k_{k_{max}} \cdot d_{max}} \tag{27}$$

In the case of spectrophotometric indication, with maximal molar absorptivity of 10^5 [$l\ mol^{-1}\ cm^{-1}$], reasonable thickness of layer $d_{max} = 5$ cm and just measurable absorbance difference of $\Delta\ A_{min}$ of 0.05 units, the change of concentration $\Delta[X]$ may still be accurately determined (cf. Proskuryakova et al.[145]). After determination of the remaining quantities — t_{max} a practical period of analysis to 10 min; $K_{k_{max}}$ a practically attainable magnitude of the rate constant of $10^8\ min^{-1}$; and Π_c an initial concentration of the reactant of 1 mol l^{-1} — the smallest determined catalyst concentration ($[K]_{min}$) for catalytic spectrophotometric techniques is calculated as follows:

$$[K]_{min} = \frac{10^{-7}}{10 \cdot 10^8} = 10^{-16}\ mol\ l^{-1} \tag{28}$$

Nevertheless, this limit has not yet been reached. The most sensitive catalytic reaction allows concentrations of 10^{-12} g $m\ell^{-1}$ to be measured,[146,147] i.e., the limit of detection at present is in some orders of magnitude worse than the theoretical value (power of detection).

There are several reasons that the limit of detection obtained in practice is significantly less than the theoretical value. The main one is the influence of the background.

b. Effect of Background

The rate of indicator reaction depends strongly on (1) the presence of impurities in the system: (2) the surface area of the reaction vessel and the presence of adsorbed substances; and (3) differences in composition of the solution under investigation and the solution used to prepare the calibration plot (variations in pH, salt composition, ionic strength, and trace substances introduced with the reagents and water). For significant background interference the total reaction rate equals the sum of two reaction rates: $v_{total} = v_{cat} + v_{background}$. The rate of the catalytic reaction is found as the difference between the total reaction rate determined experimentally and the rate of any noncatalytic reaction. The operator should minimize background variations or, at any rate, try to maintain as constant of a background as possible (small standard deviations of the blank value). By extremely clean and careful manipulation, blank value variations may be decreased but not completely avoided. Relative standard deviations about 10 to 15% must be considered normal in catalytic determinations.

Only by employing special techniques can the accuracy of catalytic determinations be increased.

Optimum working conditions are met when the known-addition technique, the method of simultaneous comparison, and catalytic titration are used.

c. Increase of Reaction Rate

The rate constant k_k of the catalyzed reaction is of particular importance for the limit of detection and virtually has a restricting affect on it, since changes by whole orders of magnitude are possible. A relative increase of the reaction rate of the catalyzed reaction as compared with the blank reaction ($v_{cat} > v_{background}$) may be realized in several ways.

Increase of temperature — The rate of a chemical reaction generally increases with an increase in temperature as predicted by the Arrhenius equation ($\log k = \text{constant} - E/4.6\ T$), where k is the reaction rate constant. Improvement of the limit of detection by an increase in temperature is, however, successful in catalytic determinations only if the rate of the catalyzed reaction increases and the rate of the noncatalyzed reaction is hardly affected by the temperature. Besides, work in far higher temperatures involves a number of practical problems. Therefore, the majority of procedures of catalytic determinations is carried out at temperatures up to 40° C.

Optimizing the conditions of the reaction — If the mechanism of a catalyzed reaction is known, the most favorable conditions of reaction for catalytic determination may be optimized, e.g., by means of the graph method.[148] Based on the mechanism of reaction ascertained in preliminary tests, the equation for the total reaction rate is found for stationary catalyst concentrations, and the time dependence is compared with that found experimentally. The procedure may be optimized when the agreement is satisfactory. This approach is exemplified by the catalytic determination of iridium and ruthenium using the reaction between Mn(III) and Hg(I).[149] The mechanism of the reaction proceeds as demonstrated by the following diagram:

$$K(III) + Mn(III) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{Mn(III) \ldots K(III)\} \qquad (29a)$$

$$\{Mn(III) \ldots K(III)\} \xrightarrow{k_2} Mn(II) + K(IV) \qquad (29b)$$

$$K(IV) + Hg(I) \xrightarrow{k_3} K(III) + Hg(II) \qquad (29c)$$

where K(III, IV) = Ir or Ru in the oxidation stage +3 and +4; k_1, k_{-1}, k_2, k_3 = reaction rate constants. From this the graph in Figure 9 (in sulfuric acid medium) may be derived. From the graph, the reaction rate may be determined by means of the following equation:[150]

$$v = \frac{K_{total}\ \Sigma\ v_i\ D_i}{\Sigma\ D_i} \qquad (30)$$

where K_{total} = the total concentration of the catalyst in all forms, v_i the formation rate of the product of reaction, and D_i the determinants derived for the various nodal points of the graph.

Accordingly, taking into consideration a few simplifications (e.g., $k_2 \ll k_3\,[Hg^I]$), one obtains from the graph (Figure 9) for the Ru-catalyzed reaction

$$v = \frac{k_1\ k_2\ [K]_{total}\ [Mn^{III}]}{k_2 + k_1\ [Mn^{III}]} \qquad (31)$$

and for the Ir-catalyzed reaction with small concentrations of Hg(I)

$$v = \frac{k_1\ k_3\ [K]_{total}\ [Mn^{III}]\ [Hg^I]}{k_3\ [Hg^I] + k_1\ [Mn^{III}]} \qquad (32)$$

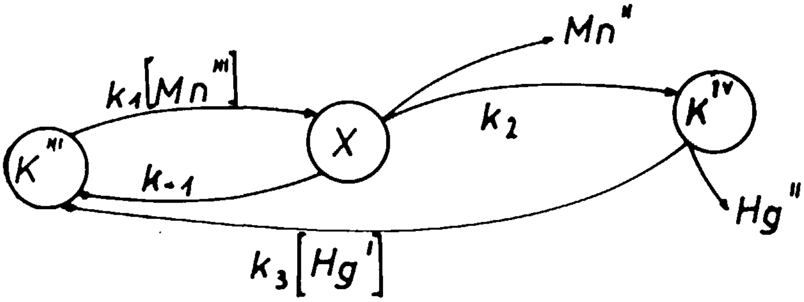


FIGURE 9. Graph for the Ir- and Ru-catalyzed redox reaction between Mn(III) and Hg(I); X = {Mn(III) ··· K(III)}.

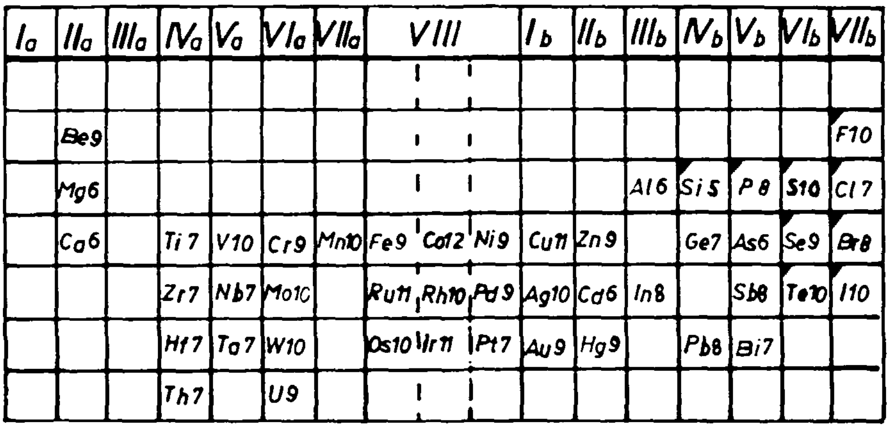
When, based on Equations 31 and 32, the most favorable conditions of reaction were selected, down to 10^{-2} μg Ir/mL and 10^{-3} μg Ru/mL may be determined. In this way Yatsimirskii et al.[151-153] succeeded in optimizing several catalytic methods of determination.

Activation of homogeneously catalyzed reactions — The best possibility of increasing the reaction rate of a catalyzed reaction is offered by the application of activators, which increase the rate of the catalyzed reaction, whereas the rate of the noncatalyzed reaction is not affected. (For details see Mottola.[38]) In a book[154] and in some surveys[138,155-157] Bontchev gives a detailed account of the theory and the analytical applications of the activation of homogeneously catalyzed reactions. Mottola[38] and Müller et al.[63] have summarized practical applications of activators for improvement of the limits of detection of metal catalyzed reactions.

Activator effects have as yet been limited to metal ion catalyzed reactions. This is connected with the strong complex-forming tendency of metal ions. Apart from the increase of sensitivity and, consequently, improvement of the limit of detection (as rule by two to four orders of magnitude), activation of catalytic reactions may still have another analytical aspect, viz. increase of selectivity by influencing the interaction between catalyst and reactant. Bontchev,[158] who was the first to propose the use of activation and masking for regulation of the selectivity of catalytic reactions, used this variant as a means of increasing the selectivity of the p-phenetidine-chlorate reaction. The indicator reaction is catalyzed by vanadium (V), iron (III), and copper (II). By use of citric acid as an activator the sensitivity of the vanadium (V)-catalyzed reaction is increased about 15-fold while the catalytic action of copper and iron is completely suppressed.

Boutchev considers that the catalytic behavior of vanadium (V) in the presence of citric acid is due to the formation of free radicals from the activator, so that the citric acid does not quench the catalytic activity of vanadium (V) even when present in large excess. The complexes of iron (III) and copper (II) with citric acid, however, are coordinately saturated and therefore no complex formation with the substrate is possible. Other examples are the catalytic determinations of silver and again vanadium.

In the first case,[159] 2,2'-bipyridyl and ethylendiamine cause activation of the silver-catalyzed sulfanilic acid-persulfate reaction and at the same time mask copper and iron. The second example[160] is the determination of vanadium by means of the p-phenetidine-bromate reaction with a high sensitivity in the presence of the activator sulfosalicylic acid which acts simultaneously as a masking agent for iron. Figure 10 gives a survey of the



Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb
	Be9															F10
	Mg6											Al6	Si5	P8	S10	Cl7
	Ca6		Ti7	V10	Cr9	Mn10	Fe9	Co12	Ni9	Cu11	Zn9		Ge7	As6	Se9	Br8
			Zr7	Nb7	Mo10		Ru11	Rh10	Pd9	Ag10	Cd6	In8		Sb8	Te10	I10
			Hf7	Ta7	W10		Os10	Ir11	Pt7	Au9	Hg9		Pb8	Bi7		
			Th7		U9											

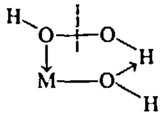
FIGURE 10. Catalytically determinable elements; numbers next to the symbols are values of detection limits, in -log c, where c = g/mL.

present state of catalytically determined elements and their limits of detection (given c in g/mℓ); activated reactions are included in the survey.

2. *Selectivity*

a. Introduction

As stated in the preceding chapter, the limits of detection of catalytic determinations are comparable with physical methods of trace analysis. As compared with other chemical methods, they are even better. Nevertheless, application of catalymetry in practical analysis is limited. The main reason is inadequate selectivity. In 1962, Bognar[161] characterized the selectivity of catalytic methods and reactions, respectively, as follows: "Besides, the catalytic effect will be more or less individual, as it rarely happens that in one and the same system still another component has a catalyzing effect. Thus catalysis is an ideal combination of two important requirements of analytical chemical reactions: sensitivity and specificity." At present we know that the selectivity of catalytic determinations is far lower as compared with physical trace analytical methods. This is due to the mechanisms of the reactions most frequently employed in catalymetry. The ability of a species to cause catalytic effects in homogeneous reactions is based on its chemical properties. Chemically similar species exhibit similar catalytic effects, and therefore selective catalytic determination in the presence of chemically related elements is not simple. This may be exemplified by the oxidation of organic and inorganic substrates by hydrogen peroxide (H_2O_2) in acidic media. The crucial step during reaction is the complex formation between the metal ion and H_2O_2, which results in loosening the O-O bonds in the H_2O_2 molecule.



Yatsimirskii[162] listed the following stages of this reaction:

$$M + H_2O_2 \longrightarrow MO_2H_2 \qquad (33a)$$

$$MO_2H_2 \longrightarrow \overset{(-)}{M}OH + OH^+ \qquad (33b)$$

Table 12
INDICATOR REACTION WITH HYDROGEN PEROXIDE AS OXIDANT

Indicator reaction	Catalysts
$H_2O_2 + I^-$	Ti, Zr, Hf, Th, V, Nb, Ta, Cr, Mo, W, Fe^{III}, $Cr_2O_7^{2-}$, PO_4^{3-}
$H_2O_2 + S_2O_3^{2-}$	Ti, Zr, Hf, V, Nb, Ta, Mo, W
$H_2O_2 + e^-$	Hf, V, Mo, W, Fe^{III}
H_2O_2 + PhOH, $PhNH_2$	Cr, Mn, Fe, Co, Ru, Os, Cu
$H_2O_2 + H_2(NHCS)_2$	Mo, W
H_2O_2 + org. dyes	Fe, Cu, Cr, Mn, Co, Ni

$$MO_2H_2 \longrightarrow \overset{(-)}{M}OH + H^+ + O \tag{33c}$$

Regeneration stage:

$$\overset{(-)}{M}OH + H^+ \longrightarrow M + H_2O \tag{34}$$

If metals are used as catalysts, which insignificantly differ in quantity, and charge their coordination tendency towards the H_2O_2 polarizing effect on the covalent O-O bond then they are comparable yielding similar effects on H_2O_2-decomposition and thus on the whole catalytic reaction. Selective determinations are only possible after modification of the testing procedure, as shown in Table 12.

Characterization of catalytic procedures as concerns selectivity is also complicated by rather blurred definitions of terms, as pointed out by Kaiser, Gottschalk, and Belcher.[163-165] In this paper, the terms selectivity and specificity are used in the sense referred to them by Kaiser.[163] The selectivity and specificity of catalytic determinations depend on the selectivity of the catalytic reaction and on the selectivity of the monitoring technique used. The determining factor of the selectivity/specificity of catalytic determinations is the selectivity of the catalyzed reaction.

The reaction rate of a (general) indicator reaction in the presence of several catalysts K_1, K_2 ... K_n

$$A + B \xrightarrow{K_1, K_2 \ldots K_n} P \tag{35}$$

may be formulated as follows:

$$v_{total} = d[P]/dt = k_1[A]^p[B]^q[K_1] + k_2[A]^p[B]^q[K_2] + \ldots + k_n[A]^p[B]^q[K_n] \tag{36}$$

If the reaction proceeds under varying conditions, a corresponding reaction rate $v_1 \ldots v_n$ is obtained for each condition (1 . . . n).

$$v_1 = k_{11}\,\Pi_{11}\,[K_1] + k_{12}\,\Pi_{12}\,[K_2] + \ldots + k_{1n}\,\Pi_{1n}\,[K_n] \tag{37a}$$

$$v_2 = k_{21}\,\Pi_{21}\,[K_1] + k_{22}\,\Pi_{22}\,[K_2] + \ldots + k_{1n}\,\Pi_{1n}\,[K_n] \tag{37b}$$

$$v_n = k_{n1}\,\Pi_{n1}\,[K_1] + k_{n2}\,\Pi_{n2}\,[K_2] + \ldots + k_{nn}\,\Pi_{nn}\,[K_n] \tag{37c}$$

where $v_1 \ldots v_n$ characterize the rates of the (total) catalytic reaction and $\Pi_{ik} = [A]^p ik[B]^q ik$ with i,k, = 1 . . . n.

A catalytic determination will be selective (Equation 36) if either the individual catalysts show, under different reaction conditions, very different catalytic activities ($k_{ii} > k_{ik}$), or the catalysts present react according to different reaction mechanisms (p_{ii}, $q_{ii} > p_{ik}$, q_{ik}).[191]

Unfortunately, not much is known about the mechanism of different catalysts in one and the same indicator reaction in most cases, thus only the sum of the effects may be considered.

When the catalyst species are not chemically similar, the selectivity of catalytic reactions is usually high. For instance, the catalytic determination of molybdenum in the presence of alkali and alkaline earth metals, cobalt, nickel, and manganese[166] or the determination of platinum metals in the presence of copper, iron, and main group elements[167] is relatively easy. Catalytic reactions are much less selective when determinant and interferent are closely related chemical species.

For example, the catalysts used in different redox reactions have some remarkable features. The same group of substances exhibits catalytic properties in reactions with different reductants and the same oxidant. In the case of oxidation of different reductants by hydrogen peroxide in an acid medium, the substances forming coordination compounds with H_2O_2 — Ti(IV), Zr(IV), Hf(IV), Fe(III), Nb(V), Ta(V), Mo(VI), W(VI) — act as catalysts (Table 12).

Reactions with halates are catalyzed by vanadium, ruthenium, rhenium, and osmium. Silver, iron, and vanadium compounds catalyze many reactions involving persulfate. A large number of oxidation reactions of arsenic (III) are catalyzed by osmium, ruthenium, and iodine compounds.

Unspecific catalytic effects are also observed with ligand exchange reactions. Thus Hg(II), Ag(I), Au(III), and Pt(IV) catalyze the substitution of a cyanide in the hexacyanoferrate(II) ion for a water molecule and may thus be catalytically determined (Asperger reaction[169]). Here the nonspecific catalytic effect is based on the common ability of forming polynuclear complexes of the type $(CN)_5$-Fe-CN-M.[154,170]

Table 13 lists some indicator reactions which are influenced in a similar way by more than one catalyst.

Most of the catalytic determination described in the literature are highly sensitive and reproducible, but their selectivity has not been considered. Therefore, they are not likely to be very useful for application to routine analysis. Change of pH, reagent concentration and temperature, use of suitable complexing agents, and selection of the best monitoring technique may greatly increase the selectivity of such catalytic reactions. Sometimes, it will not be possible to obtain sufficient selectivity by changing conditions for the catalytic reaction, and in such cases, a preliminary separation step is necessary. Such combination of separation procedure with a catalytic determination is another means of increasing the selectivity of a catalytic procedure.

b. Increase of Selectivity

i. Influence on the Catalyst-Reactant Interaction

Differences in the activities of individual catalysts in an indicator reaction are due to their specific interaction with the substrate, the oxidizing agent, the buffer, and other species present in the reaction mixture. The extent of such interactions is determined by the complex forming tendency, real potential, and other features of the catalyst, which represent conditional quantities and may be varied as desired by variation of the conditions of reaction. Thus it is possible to adjust the process of a catalytic reaction. The most important features influencing the catalytic effect are pH, reagent concentration,

Table 13
NONSPECIFIC CATALYTIC REACTION

	Reductants			
Oxidants	**I^-**	**AsO_2^-**	**ArOH**	**$ArNH_2$**
Ce^{4+}	—	Os, Ru, Ir, I	—	—
$S_2O_8^{2-}$	Ag, Fe, V	—	Ag, Fe, V	Ag, Fe, V
ClO_3^-	V, Ru, Re	—	V, Ru, Os	V, Ru, Os
BrO_3^-	V	—	V, Mo	V, Mo, Ru
IO_4^-	Ru	—	—	Mn, V, Ru, Ir

Substrate	Ligand	Catalysts
$[Fe(CN)_6]^{4-}$	H_2O	Hg, Ag, Au, Pt

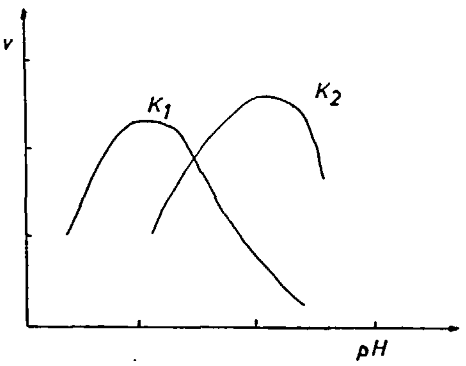


FIGURE 11. pH Dependence of catalyst behavior of two catalysts (K_1, K_2), diagrammatic representation.

and temperature. The catalytic activity of a catalyst also depends on the structure of the reactant, the coordination sphere of the catalyst, or the presence of complexing agents, which likewise may be used for increasing the selectivity of catalytic reactions.

The catalytic activity of chemical substances is often limited to a certain pH range. Frequently catalysts have an effect only within the range of a few pH units, as shown in Figure 11.

A typical case, studied by Yatsimirskii and Raizman,[171] was the reaction between iodide and hydrogen peroxide. The catalytic activities of zirconium and hafnium in this indicator reaction show different pH-dependence. Zirconium exhibits the greatest activity at pH 1.1, whereas hafnium has the greatest catalytic effect at pH 2. The reason for this behavior is the difference in stability and activity of the hydroxo-complexes of zirconium and hafnium.

The pH values for maximal formation of the complexes $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$, and $Zr(OH)_3^+$ are 0.32, 0.70, and 1.1. Catalytic activity is only exhibited by the complex $Zr(OH)_3^+$, so that the pH-dependent stability of this complex implies an analogous pH dependence of the catalytic reaction. Hafnium, compared with zirconium, forms hydroxo-complexes of different stability and the peak of its catalytic activity is shifted. If *the determination is carried out at two different pH values, zirconium and hafnium in* mixture may be determined by one and the same indicator reaction.

A similar effect was observed by Otto et al.[172] in the Co- and Mn-catalyzed tiron-H_2O_2-reaction. Whereas Mn^{2+} has the strongest catalyzing effect at approximately pH 9.5, cobalt greatly accelerates the reaction at pH 12. Due to this, manganese and cobalt may be determined together in one indicator reaction at different pH (in the presence of an activator, 1,10 phenanthroline).

The change of pH may differently influence the formation of complexes with the substrate, the oxidant, or the activator. It is well-known that copper catalyzes the oxidation of arylamines and phenols in alkaline medium, but because of the low stability of the copper complexes with ligands containing oxygen as a donor atom, only the oxidation of arylamines is catalyzed in acidic medium. Therefore, by use of phenolic substrates, other metals such as iron can be determined catalytically in acidic medium in the presence of a relatively large excess of copper.[173] Variation of pH may have a favorable effect on different reaction mechanisms which are related to specific effects of individual catalysts. The Co-catalyzed oxidation of diantipyryl-3,4,5-trimethoxyphenylmethane (redoxane) by H_2O_2 proceeds according to a radical mechanism in a medium of acetic acid. Iron and nickel, which usually interfere with catalytic oxidation with H_2O_2 in alkaline medium, may be present in excess up to 10^9-fold in this technique, as these elements are catalytically inactive due to a radical mechanism in acidic medium.[174]

The selectivity of a catalytic reaction can be changed by altering the reagent concentration, because different catalysts give rise to different kinetic dependences in the indicator reaction. An example of this, given by Worthington and Pardue,[175] was the catalytic determination of osmium and ruthenium by the Ce(IV)-As(III)-reaction.

The Ru-catalyzed reaction is not dependent on the arsenic concentration, and the reaction rate v_1 increases with rising cerium-concentration according to Equation 38. On the other hand, the rate of the Os-catalyzed reaction does not depend on the cerium-concentration, but increases with rising arsenic concentration as shown in Equation 39.

$$v_1 = \frac{4 \cdot 10^{10}\,[\mathrm{Ru}][\mathrm{Ce(IV)}]^{2.5}}{1 + 2.1 \cdot 10^{3}\,[\mathrm{Ce(IV)}]^{1.5}} \qquad (38)$$

$$v_2 = \frac{8 \cdot 10^{2}\,[\mathrm{Os}]\,[\mathrm{As(III)}]}{4.3 \cdot 10^{-3} + [\mathrm{As(III)}]} \qquad (39)$$

where [As(III)] [Ce(IV)] in mole/l; [Os(VIII)], [Ru(VIII)] in μg/mℓ. Thus, if two different ratios of As(III) to Ce(IV) are used, osmium and ruthenium are determined within the 2×10^{-10} to 10^{-7} mol l^{-1} range using the following system of equations:

$$v_1 = 240\,[\mathrm{RuO_4}] + 90.4\,[\mathrm{OsO_4}]\,(5 \times 10^{-3}\,M\ \mathrm{Ce(IV)}) \qquad (40a)$$

$$v_2 = 2.69\,[\mathrm{RuO_4}] + 78.0\,[\mathrm{OsO_4}]\,(5 \times 10^{-4}\,M\ \mathrm{Ce(IV)}) \qquad (40b)$$

where v_1, v_2 = reaction rate in mole l^{-1} s^{-1} and $[RuO_4]$, $[OsO_4]$ = concentration in mole l^{-1}.

The influence of temperature on the effect of various catalysts may also be used for increasing the selectivity of catalytic reactions, if a temperature dependence is known as represented in Figure 12.

This case was demonstrated by Wolff and Schwing,[192] who studied the catalytic oxidation of iodide by bromate. At temperatures between 0° and 40° C the reaction is catalyzed to varying extents by molybdenum (VI), tungsten (VI), and chromium (VI). The authors utilized this to develop methods for determination of binary mixtures of Mo(VI) and W(VI) and Mo(VI) with Cr(VI), by determining catalytic activities at two

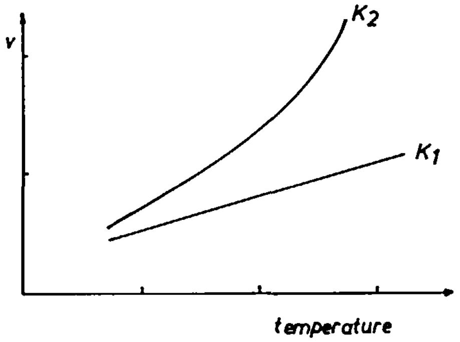


FIGURE 12. Temperature dependence of catalyst behavior of two catalysts (K_1, K_2), diagrammatic representation.

temperatures. However, because the temperature dependences of the catalytic activities are rather similar, the error in simultaneous determination is about 20%.

The first step in a catalytic reaction of a metal with the substrate is, in most cases, the formation of a complex between the metal and the substrate (see also Yatsimirskii[176]). Therefore, the coordination sphere of the catalyst as well as the state of binding and the structure of the substrate are important for the progress of metal-catalyzed reactions. Whereas the former is of particular importance if metal catalysts form inert complexes (e.g., platinum metals, cobalt), substrate structure is of particular importance when organic reactants are employed.

For example, Lukovskaya and Kushevskaya[177] found that the catalytic activities of iridium and rhodium solutions in the luminol-periodate reaction depend significantly on their history. Rhodium could be determined only in sulfate solutions because rhodium chloride solutions hydrolyze with loss of catalytic activity. On the other hand, the catalytic action of iridium is not affected by chloride and sulfate, so this reaction allows the catalytic determination of the sum of these elements in sulfate solution, whereas, in chloride solutions, iridium alone may be determined in the presence of rhodium.

A similar effect was observed by Müller et al.[91] in the reaction of Mn(III) pyrophosphate with p-benzoquinone, catalyzed by ruthenium.

In chloride medium palladium has an interfering effect at a ratio of 1:1, whereas the sulfate compounds exhibit a variety of catalytic activities and determination of Ru is possible in the presence of 100-fold excess of palladium. This effect of medium was studied in more detail by Yatsimirskii et al.[178] and was used for catalytic determination of palladium on the basis of the reaction between Mn(III) and Cl^-.

The catalytic activities of coordination compounds in reactions of the compensative type (see Yatsimirskii[176]) depend on the nature of the ligands. For example, the reaction between periodate and iodide is catalyzed by iridium compounds of the type $IrCl_{6-n}(OH)_n$[179]. The catalytic activities of the iridium compounds depend on the number of hydroxylic groups, n, in the inner sphere of complexes.

The relative catalytic activities can be expressed by the rate constants $k_o = 0$ for $IrCl_6^{2-}$; $k_1 = 1.53$ for $IrCl_5OH^{2-}$; $k_2 = 1.54$ for $IrCl_4(OH)_2^{2-}$; $k_3 = 3.07$ for $IrCl_3(OH)_3^{2-}$; $k_4 = 13.21$ for $IrCl_2(OH)_4^{2-}$.[176]

The importance of the state of binding and the structure of the substrate in redox reactions is also demonstrated in the following examples: the coordination of $S_2O_3^{2-}$ by Cd^{2+} and other ions makes impossible its oxidation by Fe^{3+} and some other oxidants.[180] The oxidation of SO_3^{2-}, $EDTA^{4-}$, $C_2O_4^{2-}$ by different oxidants is more difficult in the

Table 14
SUBSTITUTED PHENOLS AS SUBSTRATES IN THE METAL CATALYZED OXIDATION WITH HYDROGEN PEROXIDE

Substrate	Position of OH-group	Detectable Cu(II)	Concentration (μg/mL) Ni(II)	Co(II)
Quinol	Para	0.005	Inactive	0.02
Resorcinol	Meta	0.01	Inactive	0.002
Pyrocatechol	Ortho	0.05	0.1	0.0002
Pyrogallol	Ortho	0.05	0.1	0.002
Tiron	Ortho	—	0.01	0.00002

presence of the complex forming cations.[182,183] Cases are known, however, where coordination enhances the reducing ability of molecules or ions, e.g., the thiocyanate ion is oxidized more readily by bromate if this is coordinated to Fe^{3+}.[184]

Bontchev[185] proposed the use of complex formation for regulation of the selectivity of catalytic reactions. By introducing suitable substituents into the substrate, it may be possible to make it specific for some particular ion, and thus make the catalytic interaction specific. Such tailor-made substrates are known, for example, in photometric determinations, in the form of cuproins, but have not been used for catalytic determinations. However, some selectivity of substrates towards individual catalysts may be observed in the catalytic oxidation of various substituted phenols with hydrogen peroxide. These reactions are catalyzed by copper, nickel, and cobalt.[186] The catalytic action of copper is especially high if the phenol contains hydroxyl groups in the para-position, whereas meta- or ortho-substituted phenols are less suitable as substrates. Conversly nickel and, particularly, cobalt strongly catalyzed the oxidation of ortho-substituted phenols (Table 14).

To increase the selectivity of catalytic determinations, masking agents have been widely used. By masking ("internal separation"), other catalysts than the one to be determined are transformed into a catalytically inactive form. Some typical applications of masking agents are listed in Table 15.

Apart from the purposeful introduction of complex-forming agents (masking agents) into the catalyzed reaction, masking effects may also result from the reactants of the indicator reaction itself. Thus, for example, determination of copper is very specific due to its inhibiting effect on the iodine-azide reaction catalyzed by m-thioammeline, as the azide present in high concentration masks the other metal catalysts.[190] Tantalum may be determined in the presence of Nb, which has a similar catalytic effect, by means of oxidation of iodide by H_2O_2, if during preliminary treatment of the sample by the oxidizing agent H_2O_2 is masked.[187]

The choice of suitable buffers may increase the selectivity of a catalytic reaction. For example, the oxidation of Alizarin S by hydrogen peroxide in the presence of sodium hydrogen carbonate buffer is a rather unselective reaction,[188] because cobalt and manganese can both act as catalysts. In ammonium carbonate buffer, however, the reaction becomes specific for manganese because cobalt forms very stable amine complexes which are catalytically inactive. Thus, in an ammonium carbonate buffer, manganese may be determined in the presence of cobalt by catalytic titration[188] or by photometric monitoring of the indicator reaction[189] in the presence of a 1000-fold excess of cobalt.

By combined alteration of pH, temperature, reagent concentration, and simultaneous application of masking agents or activators, the selectivity of catalytic determinations may be improved.

Table 15
MASKING IN CATALYTIC ANALYSIS

Analyte	Indicator reaction	Masking agent
Mn	H_2O_2 decomposition	Sulfosalicylic acid for Fe
V	$I^- + BrO_3^-$	Citrate for Cu, Fe, Mo, Ti
Cu	$I^- + S_2O_8^{2-}$	F^- for Fe
Zn, Cd, Pb	$Ni(trien)^{2+} + Cu(EDTA)^{2-}$	Cn^- for Fe, Co, Cu, Ni
Os	Lucigenin + H_2O_2	EDTA for Co, Cu, Ni, Pb, Fe
Cr	Brompyrogallol red + H_2O_2	EDTA for Fe, Co, Ni

By choice of suitable reaction conditions, masking agents, and activators, Müller and Otto[193,194] were able to improve the selectivity of the catalytic oxidation of 1-naphthylamine by nitrate so much that the closely related platinum metals osmium and ruthenium could be determined in each other's presence. Study of the Os- and Ru-catalyzed indicator reaction in the presence of various organic complexing agents showed that the catalytic activity of osmium is influenced by these ligands, but that the activity of ruthenium is not. Use of 1,10-phenanthrline to suppress the catalytic effect of osmium allows ruthenium to be determined in the presence of osmium if 8-hydroxyquinoline is used as activator for osmium, and the concentration of the nitrate oxidant is changed. This reaction enables osmium and ruthenium to be determined when together in the concentration range of 5 to 20 ng/mℓ. The basis of the determinations is the equation system

$$\Delta A_1 = 1.63 \cdot 10^{-2}\,[\mathrm{Ru(VIII)}] + 0.162 \cdot 10^{-2}[\mathrm{Os(VIII)}] \qquad (41a)$$

$$\Delta A_2 = 1.63 \cdot 10^{-2}[\mathrm{Os(VIII)}] \qquad (41b)$$

where $\Delta A_{1,2}$ = difference in absorbance between the catalytic and the blank reaction after a reaction period of 6 min; [Ru(VIII)], [Os(VIII)] = concentration in ng/mℓ.

This method is more selective than the Ce(IV)-As(III) method[175] discussed previously (Equations 38 and 39).

ii. Combination with Separation Procedures

If the selectivity of a catalytic determination is not adequate for a given analytical problem, the procedure must be preceded by separation.

The common trace-analytical separation techniques such as liquid-liquid extraction, chromatographic methods (ion-exchange procedures, paper, and thin-layer chromatography), and co-precipitation may also be used in combination with catalytic determinations. Table 16 gives some typical applications (according to Otto et al.,[191] supplemented by more recent papers).

Liquid-liquid extraction is the technique most often used, because it is advantageous in that smaller amounts of sample are required and less time is needed for the separation step than for other techniques (e.g., ion-exchange, paper and thin-layer chromatography). Indeed, the influence of the separation matrix is also a problem with extraction methods. After an extraction, the metal is usually in an organic solvent in the presence of an excess of the extracting ligand. Because direct determination in the organic extract is not easy, the metal is often stripped into an aqueous medium. In many cases the metal can be back-extracted into water by changing the pH. However, very often the excess of ligand is also stripped from the organic phase, and it can interfere in the catalytic reaction. An additional treatment of the back-extract is then needed. Furthermore, in the

Table 16
COMBINATION OF CATALYTIC METHODS OF DETERMINATION WITH SEPARATION PROCEDURES

Element or compounds	Indicator reaction	Separation system technique	Matrix
Ni	Diphenylcarbazone + tiron + H_2O_2	I; 1-benzyldioxime/$CHCl_3$	Oxides of La, Y, P
Co	Alizarin S + H_2O_2	I; 2-nitroso-1-naphthol	P
Au	Hg(I) + Ce(IV)	I; HCl/ethyl acetate	Ores
V	Phenylhydrazine-p-sulphonic acid + ClO_3^-	I; oxine/$CHCl_3$	Blood, urine
Cr	o-Dianisidine + H_2O_2	I; HCl/MIBK	$AlCl_3$, blood
Mn	H_2O_2 dec; 1,10-phenanthroline as activator	I; PAN/$CHCl_3$	Alkali metal halides
Mo	Fe(III) + $SnCl_2$	II; Dowex 1, X-8	Sea-water
Se	Methylene blue + S^{2-}	II; Dowex 50W-X2	Water
Cr	o-Dianisidine + H_2O_2	II; Dowex 50W-X8	Industrial dust
Mn	Malachite green + IO_4^-	II, amberlite	Ta, Nb
F	Perborate + I^- (+Zr(IV)) (inhibiting action)	Microdiffusion	Biological materials
Ru	Benzidine + H_2O_2	Paper chrom.	Water
Ir	Mn(II) + BrO^-	Thin-layer chrom.	Water
Ru	o-Dianisidine + IO_4^-	Distillation as RuO_4	Ores
Cu	$Fe(SCN)_3 + S_2O_3^{2-}$	Coprecipitation on Hg_2S	Me(II,III) salts
CO_3^{2-}	Acceleration of the formation of Cr(III)-xylenol orange complex	Directional crystn. of an aq. salt soln of eutectic compn.	CsI

Note: I = liquid-liquid extraction; II = ion-exchange; PAN = 1-(2-Pyridylazo)-2-napthol.

back-extraction, some of the organic solvent may be introduced into the aqueous phase, where it may cause inhibitory effects. The metal complex may alternatively be transferred to an aqueous phase by oxidative destruction of the organic extract. Any alteration of the extract, however, involves prolongation of the period of analysis and may include losses and contamination. It is therefore often tried to determine the species separated by extraction directly in the organic extract. This is possible by means of extractive catalytic methods of determination.[191]

Extractive catalymetric methods of determination, by analogy with extractive spectrophotometric methods, are to be understood as a technique of analysis in which the catalyst (inhibitor, activator) is separated by liquid-liquid extraction and in which the catalyst (inhibitor, activator) is determined directly in the organic extract. For catalytic determination of a species (in most cases, a metal ion) in an organic extract the following conditions must be fulfilled:

1. The metal species extracted must be catalytically active in the indicator reaction when this is carried out in mixtures of water and organic solvents or in purely organic solvents.
2. The extraction system should enable the metal of interest to be separated specifically without coextraction of interfering extracting agents.

By means of these extractive catalytic methods of determination, it was possible to work out highly selective and sensitive methods of analysis. Using the Ag-catalyzed Brompyrogallol Red (BPR)-Potassium persulfate reaction, Müller et al.[40] determined nanogram amounts of silver after extraction of the silver with 1,10-phenanthroline and BPR in nitrobenzene in a dioxan-water mixture. The attraction of extractive catalytic methods is illustrated further by Otto and Müller[195,196] by a method for the determination of iron. The selectivity of the indicator reaction used — the p-phenetidine-H_2O_2 reaction — is rather low because cobalt, nickel, and copper interfere.[197] An extractive catalytic procedure based on the same indicator reaction, and extraction of iron from 7 *M* lithium chloride by methyl isobutyl ketone (MIBK) allowed iron to be determined in salts of cobalt, nickel, and copper in the range 5×10^{-6} to 5×10^{-3}% iron with relative errors of about 2 to 10%.

An extractive catalymetric determination of molybdenum in sea water was worked out by the same authors, which based on the catalytic oxidation of 1-naphthylamine by bromate.[198] Modybdenum is extracted as MoO_2 (oxine)$_2$ with chloroforme and the extract is directly applied in the reaction mixture. The method enables molybdenum to be determined down to 2.7×10^{-9} *M*. The relative error of the determination is 10%. 10^{-4} *M* V, 2×10^{-4} *M* Cr, 5×10^{-5} *M* W, and 10^{-2} *M* Mn, Ni, Cu, Co, Fe, Mg, Zn, Cd, Al, and Pb cause no interference. Mechanistic investigations showed that in the reaction mixture MoO_2 (oxine)$_2$ dissociates completely to catalytically active MoO_2^{2+}.

An example of a catalytic indicator reaction in organic medium suitable for an extractive catalytic procedure is the method developed for determination of copper based on the oxidation of sulfanilic acid by hydrogen peroxide.[200] Copper was extracted into chloroform as a ternary complex with pyridine and salicylate.[201] This method could be employed for the determination of copper in liver tissue and in liver biopsy samples.[202] The method enables copper to be determined in liver biopsy samples of about 5 mg dry weight by use of a simple spectrophotometer and can be used in diagnosis of Wilson's disease.

An extractive catalymetric procedure for the determination of Cr (VI) based on the reaction between o-dianisidine with H_2O_2 was worked out by Müller et al.[203] Chromate is extracted from hydrochloric solution with MIBK as $\{MIBKH^+, HCrO_4^- \cdot 7\ MIBK\}$, and the extract is applied in a water/ethanol/reactant mixture. In this manner chromium may be determined between 3 and 30 ng/mℓ in the reaction mixture. The method was applied with success for chromium determination in blood (20 to 300 ng Cr/mℓ).

An extractive catalytic method for the determination of dimethylglyoxime after extraction with n-butanol, which is based on the reaction pyrocatechol/H_2O_2/Co(II) was worked out by Antonov and Kreingold.[204]

D. Application of Catalytic Methods of Analysis

Catalytic methods for determination of traces were highly successful in the analysis of high-purity substances and materials, biological matrices, materials of environmental relevance, geological samples, and water.

The high power of detection of catalytic methods of determination permits determination of traces in minimum sample quantities. This is particularly advantageous in the analysis of biological and geological samples.

The high sensitivity of catalytic effects is the reason for the increasing use made of catalytic reactions as a basis of reaction detectors in liquid chromatography.[417] The low limits of detection of chemiluminescence reactions (e.g., metal-catalyzed oxidation of luminol) make this system of interest for metal-ion detection in liquid chromatography since the reaction is catalyzed by at least 20 metal ions.[38] A new principle for high-performance (liquid-performance) liquid chromatography is described by Nachtmann et al.,[418] in which the separation column is coupled to a catalytic detection system. The catalytic reaction is based on the Ce(IV)/As(III) reaction, which is catalyzed by iodide. The reaction was studied for continuous operation using triiodothyronine as substrate. The limit of detection for the hormones tetra- and triiodothyronine are in the subnanogram range. Lankmayr et al.[419] used the catalytic detection principle in HPLC for the determination of enantiomeric thyroxines in serum: the same authors[420] also reported the application of a catalytic detection principle for trace determination (5 to 9 ng) of iodine containing compounds by HPLC.

It must, however, be considered in all analytical problems that as a rule the selectivity of catalytic determinations is not very high.

Very favorable conditions are found in the determination of traces in high-purity substances and materials by means of catalytic methods, as all further contaminations likewise occur only in the same range, which nearly excludes interferences. The influence of the matrix on the catalytic determination of traces must be excluded by preliminary tests. If the matrix interferes, separation is necessary. Matrix component which may be transferred to a volatile form can be easily and completely separated. Manganese may be determined in sulfur[205] or selenium[206] after oxidation of the chalcogenes. Copper may be determined in germanium after separation of the latter in the form of $GeCl_4$. Determination of manganese[207] and chromium[208] in SiO_2 is possible after volatilization of Si in the form of SiF_4.

The amounts determined in high-purity substances by means of catalytic methods range between 10^{-7} and 10^{-4}%. In biological materials the majority of catalytically well-determinable transition metals is present in similar orders of magnitude. Due to this fact, selectivity of the catalytic determinations is often sufficient and permits determination of traces without additional separation procedures.

Water has proved a very favorable matrix for catalytic determinations. For solving geochemical, biochemical, and environmental problems, investigations into the content of trace elements in sea water, in rivers, lakes and ponds, and in ground water and tap water, for the control of technical equipment in boiler and reactor water, are of vital importance.

By employment of sensitive catalytic methods, time consuming concentration procedures may often be avoided and small sample volumes may be used. As concerns selectivity, catalytic determinations meet the demands on analytical procedures for examination of natural waters, since the transition metals, which are of particular catalytic activity, are present in low concentrations. Interfering iron contents may be masked with fluoride.

A detailed survey of applications of catalytic methods of determination is given by Müller et al,[63] and procedures and possible errors are discussed in a few examples of application. Tables 17 through 19 also give surveys of applications, article reviews, new catalytic methods for determination of metals and nonmetals, and new concepts in the field of catalytic methods.

Table 17
APPLICATION OF CATALYTIC METHODS

Substance, material, or element	Where found	Ref.
	High-Purity Substances, Materials, and Industry Products	
Cobalt	Ni	174, 219
	P	220
	Alkali metal halides	221, 222
	Mo, W	223
	Al, Ga, Tl, Nb, Ba	25
Copper	Glass	25, 214
	HCl	215
	Acetic acid, NaN_3	190
	Zn	217
	Sb, Cd, Nb, Al, Zr, Na_2 SO_4	25
Iron	Glass	214
	Co-, Ni-, Cu-salts	195
	Alkali metal halides	222, 224
	Cd	225
Chromium	SiO_2, KCl, Sb, $LiIO_3$	208
	Al	25, 227
	$BaCO_3$, K_2, CO_3	25
	GaAs	228, 229
	Mo, W	230
Manganese	Se	206
	Ta, Nb	205
	S	233
	Si	207
	Zn, Cd	235
	HNO_3	25
	Alkali metal halides	236
Nickel	La, Y	237
	Ta, Nb	238
	P, Sb, W	25
Osmium	Ru, Se, Te, Re	239
Silver	Pb	210
	Cd, Zn	211
	AgI	212
	Zn	213
Sulfur	Cu-, Ag-, Au-, Zn-, Cd-, Hg-sulfides	240
Vanadium	Al	241
Ru	Cu-Ni-sulfides	311
	Gaseous Cl_2, NaOH soln, Hg, other materials in Cl_2 production	312
Fe, Cu, Mn	ZnS	313
Fe	Pure ammonium, alkali metal salts	314
Cu, Fe	Spectrally pure salts	315
Ti, Au	Specially pure $SiCl_4$	316, 317
Ti	$(MeO)_4Si$	318
Mo, W	Highly pure compounds	319
Carbonates	High-purity alkali metal halides	320
Ir, Ru	Pt, Pd, their salts without matrix sepn	357
Mn	Nonferrous alloys	364
	Biological and Environmental Materials	
Ag	Saliva	242
Al	Plants	155

Table 17 (continued)
APPLICATION OF CATALYTIC METHODS

Substance, material, or element	Where found	Ref.
As	Lung tissue	244
Co	Milk	245
Cr	Plants, liver, serum	246
Co	Urine	247
Cu	Serum	248—250
	Liver	202
	Pharmaceutical products	190, 253
F^-	Plants	254
Iron	Serum	255
	Plants	256, 257
Hg	Urine, serum	258, 259
	Fish	258
Iodide	Hormones	260, 261
	Plants, soils, liver	262
	Serum	263
	Urine	264
	Thyroxine	265
	Urine	266
Mg	Blood	267
	Plants	155
Mo	Plants, milk	269, 270
NH_3	Wood	271
Oxalic acid	Blood, urine	272
V	Plants, liver, other materials	273, 274
	Blood, urine, blood plasma	275
Zn	Plants	155
Total iron-binding capacity of blood serum and iron	Biological materials	327, 328
	Water Analysis	
Amino acids	Natural water	276
Co	Reactor water	277
	Drinking water	278
Cr	Several waters	279
Cu	Pure water	190
	Boiler feed water	281
	Sea water	282
	River water	279
Fe	Drinking water, boiler feed water	224, 284—286
	River water	257, 279
Hg	River and drinking water	259
I^-	River water	287
	Natural water	288
Mn	Sea water, several waters	289, 290
Mo	Sea water	198, 292—294
	Drinking water	295
NH_3	Natural water	271
V	River, sea water	296
	Drinking water	297
	Pure water	241
Mn	Natural waters	321
Re	Ocean water	322
Hg	Waters of elec. stations	323
W	Mine waters	324

Table 17 (continued)
APPLICATION OF CATALYTIC METHODS

Substance, material, or element	Where found	Ref.
	Geological Objects	
Ag	Granite	298
Au	Ores	299
Br^-	Rocks	300
Cr	Rocks, ores	301
	Industrial dust	302
Hg	Dust	303
I^-	Soils	304
Mo	Rocks	292
Ni	Minerals	305
Os	Rocks	306
Re	Rocks	307
Ru	Ores	308, 309
V	Rocks	310
Ir, Rh, Pd	Rocks	326
Fluoride	Rocks, soils	383

Table 18
SELECTED BOOKS AND REVIEWS ON KINETIC (CATALYTIC) METHODS OF ANALYSIS

I. Books
  A. Yatsimirskii, K. B., *Kinetic Methods of Analysis*, 1st ed., Oxford, 1966
  B. Mark H. B. and Rechnitz, G. A., *Kinetics in Analytical Chemistry*, New York, 1968
  C. Costache, D., *Chemical Analysis with Kinetic Methods (Rum.)*, Bukarest, 1974
  D. Mueller, H., Otto, M., and Werner, G., *Katalytische Methoden in der Spurenanalyse*, Leipzig, 1980

II. Reviews (1976—1980), author, year of publication, comments, references
  A. General reviews
    1. Weisz, 1976, use of catalyzed reactions in analytical chemistry, application to open kinetic systems[331]
    2. Mueller and Werner, 1976, comprehensive review of catalyzed reaction methods, determination of platinium metals, automation of catalytic methods[332]
    3. Guilbault, 1978, application of kinetic and catalysis to analysis, reaction rate calculations, monitoring reaction rates, analytical applications[134]
    4. Yatsimirskii and Tikhonova, 1977, catalytic methods of analysis, basic remarks, and some indicator redox reactions[333]
    5. Dolmanova, *1980*, enzymatic methods of determining organic and inorganic methods are reviewed (198 Ref.)[421]
    6. Blaedel and Boguslaski, 1978, chemical amplification in analysis, amplification by catalysis, cycling, and multiplication[23]
  B. Reviews concentrating on catalytic applications
    1. Nabivanec and Kalbina, 1977, kinetic methods for the analysis of natural waters[335]
    2. Dolmanova and Peshkova, 1977, catalyzed redox-reaction for the determination of organic substances and nontransition metals[336]
  C. Catalytic titrants and end-point indication
    1. Hadjiioannou, 1976[64]
  D. Miscellaneous
    1. Otto, Mueller, and Werner, 1978, selectivity of catalytic methods, theory, possibilities of increase of selectivity, extractive catalytic determinations[191]

Table 19
CATALYTIC METHODS FOR THE DETERMINATION OF METALS AND NONMETALS PUBLISHED BETWEEN 1978 AND APPROXIMATELY JUNE 1980

Species	Indicator reaction	Comments	Ref.
Metals			
Arsenic	Enzymatic method	0.02 to 0.2 μg/mℓ in drinking water and river water, turbimetric method	337
Bismuth	Plumbite + sodium stannite	Turbimetric method	338
Cobalt	Oxidation of gallic acid	Indirect kinetic method	339
	Co(II) and Hg(II) in the presence of DCTA	Spectrophotometric determination of Co(III)-DCTA complex	340
	Gallocyanin + H_2O_2	0.2 to 2.4 ng/mℓ apparent molar absorptivity	341
	Quinalizarin + H_2O_2	1×10^{-8}—2×10^{-7} M	422
	1-4-Dihydroxyanthraquinone	3 ng/mℓ; s = 4.2—15% for 5—30 ng Co/mℓ	423
Copper	Hydroquinone + H_2O_2	1.5×10^{7} mol^{-1} cm^{-1} 1—2×10^{-4} μg/mℓ, aqueous-organic media	342
	Inhibition of the iodine/azide reaction	1—50 μg Cu/50 mℓ; 2—20 μg Zn/50 mℓ	343
	N,*N*-dimethyl-p-phenylenediamine + $PhNMe_2$ + H_2O_2	Cu(II) catalyzes the oxidation of Bindschelders green	344
	Ce(IV) + I^{-1}	Cu^{2+} and Ni^{2+} in trace (?) amounts; (10^{-3} M) were determined	345
	Amidol + H_2O_2	5×10^{-4} μg/mℓ in the presence of H_3BO_3, determined in zinc sulfide (3×10^{-6}—3×10^{-5}%)	313
	2,2′-Diquinoxalyl + Sn(II); Ti(III)	10^{-5}—10^{-4}% Cu and Fe were determined in spectrally pure salts	315
	Hydroquinone + H_2O_2	Cu(II) was determined in large excess of Fe(II, III)	346
	Sulfanilic acid + H_2O_2	10—350 ppm Cu in liver biopsy samples after extraction of Cu(II) as salicylatepyridine complex	202
	$S_2O_8^{2-}$ + Br^- + ascorbic acid (Landolt reaction)	0(?)—1 ppm in dissimilar samples	348
	Autooxidation of 2,2′-dipyridylketone hyrazone	Fluorimetric determination of Cu and Hg, Cu(II) 0.4—1 ppb; Hg(II) 80—320 ppb	424
	Oxidative coupling reaction of *p*-hydrazinobenzene sulfonic acid with m-phenylenediamine	ng Amounts of Cu(II)	425
	2-Thiosemicarbazone of Na 1,2-naphtoquinone-4-sulfonate + H_2O_2	0.25 ng Cu/mℓ; s = 4.8—18.2% for 0.8—5 ng Cu/mℓ	426
	p-Anisidine + N,*N*-dimethylaniline (variamine blue B leucobase) + H_2O_2	10^{-8} M Cu(II)	427
	Hydroquinone + H_2O_2	Effects of some organic solvents were examined; $(4 \pm 0.6) \times 10^{-6}$ μg Cu/mℓ method was used for determination of $(2 \pm 0.6) \times 10^{-4}$ μg Cu(II)/mℓ in blood serum after albumen separation	428
Chromium	*o*-Dianisidine + H_2O_2	(4.9 ± 0.7) 10^{-5} μg Cr/mℓ, organic-aqueous media, role of DMF in increased Cr catalytic activity is discussed	347
	IO_4^- + As(III)	Cr (10—100 ng), Os (1—10 ng); Cr was detected in ores	349

Table 19 (continued)
CATALYTIC METHODS FOR THE DETERMINATION OF METALS AND NONMETALS PUBLISHED BETWEEN 1978 AND APPROXIMATELY JUNE 1980

Species	Indicator reaction	Comments	Ref.
		Metals	
Germanium	MoO_4^{2-} + Sn(II)	3—8 × 10^{-2} μg Ge/mℓ; forming of molybdogermanate blue	350
Gold	Molybdophosphate acid + formic acid	(1.0 ± 0.2) × 10^{-2} μg/mℓ; method was used for determining 2 × 10^{-7}% Au in special purity $SiCl_4$	351
	Iodine/azide reaction in the presence of 2-mercaptopurine	Au(III), 100 ng/5 mℓ; Os(VIII), 25 ng/5 mℓ; Ru(VIII), 10 ng/5 mℓ	352
Iridium		10^{-5}—10^{-7}% Ir, Rh, Pd in rocks without separation	326
	N-methyldiphenylamine-4-sulfonic acid + NH_4VO_3	Limit of detection for Ir(IV) 2 × 10^{-10} g/mℓ	353
	p-Chlorobenzoic acid 5-bromo-salycidenehydrazide + KIO_3	Detection limit for Ir 2 × 10^{-3} μg/5 mℓ; Cr, Mn, Ru, Os also catalyze the reaction	355
	Cu(II) tellurate + hypobromite	5 × 10^{-4} μg/mℓ; tenfold excess Rh, Cr interfere	355a
	Photodecomposition of IO_4^-	80—800 ng Ir; relative S.D. 1.8%	356
	Luminol + H_2O_2	Ir 10^{-2} μg (S.D. 0.003 μg); determination of >10^{-3}% Ir, 10^{-4}% Ru in Pt, Pd, and their salts without matrix separation	357
	Direct blue GB + H_2O_2	Ir and Ru were determined in concentration of 10^{-4}—10^{-3}%	358
	IO_4^- + Cu(II)	0.00014 ppm Cu(II); s < 5%	429
	Ce(IV) + As(III)	Cat. effect of Ir-H_2SO_4 complexes	430
Iron	*p*-Phenetidine + H_2O_2	Determination of the total iron-binding capacity of blood serum, only 0.05 mℓ serum is necessary	327
	p-Phenetidine + H_2O_2	Rapid, simple, and reproducible method for determination of Fe in biological material	328
	p-Phenetidine + H_2O_2	5—140 ng Fe/mℓ; flow-stream analyzer; 30 samples per H, S.D. 5%	284
	p-Anisidine + N,N-dimethylalanine (+ H_2O_2 → blue compound)	6—20 ng Fe/mℓ; contents of Fe in pure ammonium and alkali metal salt were determined (10^{-4}—10^{-5}%)	314
	p-Aminophenol + H_2O_2	0.5 × 10^{-1} up to 4.5 × 10^{-2} μg/mℓ; relative mean error ± 1.6%	359
	H-acid + H_2O_2	3 × 10^{-6}—10^{-5}% Fe in ZnS	313
	Perbromate + I^-	Kinetic study of the iron(II)-induced perbromate-iodide reaction with an iodide-ion-selective el., determination of Fe, BrO_4^-, EDTA, and other aminopolycarbonic acids	402
	Erioglaucine A + h · r	Substrate undergoes discoloration when irradiated by photons of λ <360 nm	360
	Anisole + H_2O_2	Process based on the GC measurement of *o*-hydroxyanisole, which is a product of the reaction; detection limit 0.25 ppb linear to 1000 ppb; Fe determination in river water and vitamin tablets	431
Mercury	Hg + CuDEDTC → Cu, H_2O_2 + hydroquinone	0.005 μg/mℓ; indirect determination	361

Table 19 (continued)
CATALYTIC METHODS FOR THE DETERMINATION OF METALS AND NONMETALS PUBLISHED BETWEEN 1978 AND APPROXIMATELY JUNE 1980

Species	Indicator reaction	Comments	Ref.
		Metals	
	o-Diannisidine + H_2O_2 peroxidase inhibition by Hg	10^{-5} μg Hg/mℓ; Bi, Cd show the same inhibiting action	362
	$H_3[P(Mo_3O_{10})_4]$ + NaH_2PO_2	10^{-3} μg/mℓ; mechanism of the catalytic action of mercury is suggested	363
	Mn(II) + α, β, γ, δ-tetraphenylporphine sulfonate	Hg(II) accelerated the complex formation; 10^{-8} *M* Hg(II); method is highly selective	432
Manganese	H-acid + H_2O_2	Mn in the 3×10^{-6} to 1.5 to 10^{-5}% range in zinc sulfide	313
	Periodate + Sb(III)	Automatic spectrophotometric method; Mn 10^{-8}—10^{-6} *M*; indirect NTA, EDTA, DTPA at the 10^{-7}—10^{-6} *M* level	364
	Lumomagneson + H_2O_2	4.4×10^{-4} μg/mℓ in neutral media	365
	Periodate + acetylacetone	Mn was determined in natural waters	321
	Enzymatic oxidation of 2,3-diketogalonate	Fluorometric technique, detection limit 8 μ *M* Mn(II)	366
	p-Fuchsin leuco base + IO_4^-	NTA as masking agent; 2×10^{-3} μg Mn/mℓ; $S \leqslant 0.15$ for 2×10^{-6}% Mn; determined in prod. for fiber optics	433
Molybdenum	I^- + H_2O_2	Automated method, determination of Mo in plant materials, 0.01 ppm using 0.25-g sample	367
	Se(IV) + Sn(II)	Physiological conc. of Mo are determined in 10 mℓ of ashed human blood or plasma and 1 mℓ of ashed urine	330
	Hydrazine sulfate + methylene blue	3 ng Mo/mℓ in 10^{-3} *M* wet solution	434
	H_2O_2 + I^-	2×10^{-7} *M*; $s \leqslant 0.08$; Mo(VI) and W(VI) was determined in the presence of each other without preseparation	435
Niobium	*o*-Aminophenol + H_2O_2, pyrogallol, gallic acid	(1—3) × 10^{-4} *M* Nb, (0.5—2) × 10^{-7} *M* Ta, Nb and Ta were determined in $(MeO)_4Si$	318
Nickel	Luminol + H_2O_2	Chemiluminescence method; 0.5 ng Ni/mℓ; S.D. 6 ng Ni/mℓ = 2%	368
Osmium		Reproduction and sensitivity of a catalytic method for determining Os in Cu-Ni ores were studied	369
	Arsenite + periodate	Os(VIII, VI, IV); det. limit 5×10^{-7} μg/mℓ! Ds determination (0.0011—0.0057 g/t ore)	436
	p-Chlorobenzoic acid + 5-bromosalicylidenehydrazide	Chemiluminescence reaction; det. limit μg/5 mℓ: Ir 2×10^{-3}; Mn 2.5×10^{-2}; Cr 10^{-2}; Ru 5×10^{-2}; Os 4×10^{-2}; s = 0.10—0.12	437
Palladium	Toluidine blue + hypophosphite	0.2—5 ppm Pd^{2+}; heterogenous reaction	370
	Pentacyanoammineferrate + nitroso R salt	0.04—1.2 ppm	371
	Cyanoammineferrate + nitroso R salt	Ligand exchange; 0.04—1.2 ppm; Fe(III), Hg(II), Au(III), Ag(I) interfere	438
Rhenium	Malachite green + thiourea	Method was used to determine Re in Cu-Zn ores of complex composition	325
	Na_2TeO_4 + $SnCl_2$	Average conc. of dissolved Re in ocean water was 0.009 μg/ℓ	322

Table 19 (continued)
CATALYTIC METHODS FOR THE DETERMINATION OF METALS AND NONMETALS PUBLISHED BETWEEN 1978 AND APPROXIMATELY JUNE 1980

Species	Indicator reaction	Comments	Ref.
Metals			
	Hydrolysis of α-furildioxime	0.005—0.5 μg/mℓ; Re content in Cu ores and in rocks was determined	372
	Malachite green + $SnCl_2$	1.86×10^{-3} μg Re/mℓ; with citric or tartaric acid as activator 1.86×10^{-5} μg Re/mℓ	439
Rhodium	$Cu(OH)_4^{2-} + H_4TeO_6^{2-} + BrO^-$	2×10^{-3} mg/mℓ, Fe, Cr, Pb, Bi, Ir, and other elements	373
	Ag(I) + Fe(II)	10^{-4}—6×10^{-4}%, heterogenous reaction	374
Ruthenium	Tropeolin OO + KIO_4	4×10^{-6} μg Ru/mℓ, Ru was determined in products of Cu-Ni sulfide are processing contg. 10^{-6}—10^{-5}%	311
	Luminol + H_2O_2	Ru was determined in gaseous Cl_2, NaOH solutions, Hg	312
Silver	Silver was detd. in gold, 1.4×10^{-2} $AuCl_4^-$ was extracted		375
	$[Fe(CN)_5NH_3]^{3-}$ + ferrozine	Substitution reaction; Hg^{2+} (10 ppb), Ag^+ (20 ppb), Au^{3+} (100 ppb) was detd., S.D. <5%	376
	Indigo carmine + $K_2S_2O_8$	Ag(I) 0.3—4.0 μg/mℓ	377
Tellurium	Fe(III)-tartaric acid + $SnCl_2$	Te(IV) 0.006—0.030 μg/mlℓ	378
Titanium	*o*-Phenylenediamine + H_2O_2	$(5 \pm 0.4) \times 10^{-4}$ μg Ti/mℓ, method was used to determine Ti in specially pure $SiCl_4$	317
Vanadium	$KBrO_3$ + KBr	V (0? to 0.6 ppm)	
Tungsten	*o*-Aminophenol + H_2O_2	Mo and W were detd. in the presence of each other at ratios < 10:1; method was used to det. W and Mo in highly pure inorganic compounds	319
	H_2O_2-I^--ascorbic acid (Landolt reaction)	Method used for W determination in mine waters	324
Zinc	Resorcinol + H_2O_2 (or autooxidation)	0.9—8.0 ppm, s ~ 10%	440
Rare earth metals	*p*-Phenetidine + IO_4^-		441
Platinum group elements	Direct blue 6B + oxidants	Ir and Ru; 10^{-4}—10^{-3} and 10^{-2}%	442
Nonmetals			
Bicarbonate	Formation of the Cr-EDTA complex	100—800 ppm $NaHCO_3$	443
Borate	Hydrolysis of *N*-nitroso-hydroxylamine-*N*-sulfonate	Hydrolysis is followed by monitoring of the sulfonate absorbance at 258 nm; no interference by anions has been observed	382
Carbonate	Complexion of Cr(III) with xylenol orange	$\geq 5 \times 10^{-4}$% CO_3^{2-} in very pure KBr and CsI and $\geq 10^{-3}$% CO_3^{2-} in KCl was detd.	320
Chlorine	$Fe^{2+} + ClO_3^-$	Det limit 10^{-1} μg/mℓ; s = 7.3%; Cl was detd. in rocks	444
Fluoride	Ce(IV)/As(III) reaction + I^- (F^- as inhibitor)	10—100 ppm F^-	445
	Inhibiting effect on the zirconium-catalyzed reaction between perborate and iodide	Fluoride is separated from the matrix by diffusion; method is applied to the analysis of geschemical mat., rain water, and aerosol filter samples	383

Table 19 (continued)
CATALYTIC METHODS FOR THE DETERMINATION OF METALS AND NONMETALS PUBLISHED BETWEEN 1978 AND APPROXIMATELY JUNE 1980

Species	Indicator reaction	Comments	Ref.
		Nonmetals	
	$H_2O_2 + I$	Catalytic titration, F^- with $Th(NO_3)_4$, 3.7 mg NH_4F, 5.5 mg KF, and 4.3 mg Na_2SiF_6 were detd., average deviation ~0.9%	384
Iodide	2-Thiosemicarbazone-1,2. napthaquinone-4-sulfonate + H_2O_2	I^- 0.5—4 μg/mℓ	
	Ce(IV) + As(III)	Method for the accurate catalytic determination of trace iodine in inorganic and organic materials	460
	$CH_3COH_3 + I_2$	I^- 1—10^{-5} *M*; iodide-selective el.	408
	Chloramine-T + H_2O_2	I^- 1.59—9 μg; chloramine-T selective el.	283
	$H_2O_2 + I^- \xrightarrow[\text{peroxidase}]{}$	0.7—9.2 mg in the presence of other halides, enzymatic enthalpimetry	386
EDTA (α-aminopolycarbonic acids)	*p*-Phenetidine + H_2O_2 (inhibitory effect on the iron-catalyzed reaction)	Tetra-, penta-, and hexa-aminopolycarbonic acids were detd. from 2.5×10^{-7}—2.5×10^{-6} *M*	137
	1,4-Dihydrooxyphthalimide-dithiosemicarbazone + aerial oxygen (inhibitory effect on the Mn(II)-catalyzed reaction	Semiautomatic spectrophotometric method, catalytic titration 750—4000 μg/range	387
Oxalic acid	Aromatic azo compounds + chromic acid	Oxalic acid in microgram concentrations	388
	Thiazine dyes + $TiCl_3$	Oxalic acid 6 μg/mℓ, commonly occurring anions do not interfere	389
Phosphate	Heteropoly blue formation	Phosphate (0.08—1.16 μg/mℓ) and silicate (12—60 μg/mℓ) can be detected simultaneously; catalytic reaction?	390
Sulfur and sulfur-containing compounds	Iodine/azide reaction	Elemental S ~ 90 ppm was detd. titrimetrically in carbonates such as $S_2O_3^-$	
	Decomposition on $KBrO_3$	SCN^-, $S_2O_3^{2-}$, SO_3^{2-}, S^{2-} catalyze; $KBrO_3$ decompn. in acid medium; SCN^-—0.005 μg/mℓ; $S_2O_3^{2-}$—0.009 μg/mℓ; S^{2-}—0.006 μg/mℓ; SO_3^{2-}—0.01 μg/mℓ	392
	$VO_3^- \rightarrow V(IV)$	VO_3^- is reduced to V(IV) by S_2^-, SO_3^{2-}; chemiluminescence effect	393
	Iodine/azide reaction	Acetone or DMF were used for the extraction of sulfur from rubber; 3—75 μg S/50 mℓ was detd	394
Nitrogen-containing compounds	Hydroquinone/H_2O_2 + Cu(II), activator or inhibitor action	Detn. of pharmaceuticals in animal blood nonalbuminous plasma	446
Phosphorous-containing compounds	Hydroquinone/H_2O_2 + Cu(II); *o*-dianisidine/H_2O_2 + Cr(III); inhibitor action	10^{-9}—10^{-8} *M*; in P-cont. complexones	447
Sulfur-containing compounds	*o*-Dianisidine/H_2O_2 + peroxidase; inhibitor action	=S, –SH cont. groups and heterocyclic sulfur; 10^{-8}—10^{-4} *M*	448

Table 19 (continued)
CATALYTIC METHODS FOR THE DETERMINATION OF METALS AND NONMETALS PUBLISHED BETWEEN 1978 AND APPROXIMATELY JUNE 1980

Species	Indicator reaction	Comments	Ref.
		Nonmetals	
	$H_2O_2 + S^{2-}$; peroxidase (rhodamine B and fluorescein as sensitizers)	S^{2-} was detd. at 0.1 ng/mℓ; chemiluminescence	449
	$NaN_3 + I_2$	S^{2-} was collected on basic Zn-carbonate	450
EDTA	V(V) + 2-amino-4-methylphenol ($NaClO_3$)	Tensametric determination; oxidation reaction is inhibited by EDTA; 0.015—0.29 μg EDTA/mℓ	451
H_2O_2	2,4,5-trichloro-6-carbopentooxyphenol-oxalate + H_2O_2 (in presence of Et_3N)	Chemiluminescence reaction; det. limit 2×10^{-8} *M*; linear to 10^{-3} *M*	452
Thiourea/thiocyanate	$NaN_3 + I_2$	Different induction effects of thiourea and SCN^-; thiourea 1.6×10^{-8} and SCN^- 2—12 $\times 10^{-8}$ g/mℓ; s < 3%	453
		New Methods and Concepts	
	Competitive reaction systems	Determination of phosphate	54
		Determination of catalytic activity of *N*-benzoylthiourea derivatives	55
		Determination of catalytic activity of *N*-benzoylseleno ureas	62
	Reactants are dissolved in two immiscible liquid phases	Simple method for kinetic-catalytic determinations; with the iodine/azide reaction $S_2O_3^{2-}$ was detd., copper acts as catalyst for the decomposition of H_2O_2	395
	Open systems	UV-absorptiostat, determination of catalase, ascorbate oxidase, peroxidase, sorbitol, dehydrogenase, lactate dehydrogenase	47a
		pH-stat method to metal ion-catalyzed reactions	51
	Sample injection in closed-loop flow systems	Catalysts (enzymes or metal ions) were detd. in closed-loop systems; successful removal of the enzyme glucose oxidase (by physical adsorption) and copper ions (by controlled electrode-position)	396
	Double indication	The iodine/azide reaction catalyzed by S containing compounds was followed simultaneously by optical and thermometric measurements in closed and flowing systems	400
	Chromotropic acid + BrO_3^- (flow injection technique)	0.3—4.8 ng (10—160 ppb) V(V); 60 samples H; spectrophotometrically monitoring	454
	$H_2O_2 + I^-$ (flow injection technique)	20—3000 ppb Mo(VI); 60 samples/h; flow-through ion selective electrode; difference potentiometric principle	455

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