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OF SCIENCE FRONTIER RESEARCH: B

Chemistry

Study of Stannous-Cerium

Mass Spectrometry Method

Highlights

Binary Reaction System

Microextraction Based Gas

Discovering Thoughts, Inventing Future

Volume 13

Issue 6

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CHEMISTRY



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Evaluation of the Uncertainty of Measurement

By Valcan Angela

Abstract - This paper presents the calculation of uncertainty of measurement to determine total phosphorus in water by spectrophotometric method. For evaluation of uncertainty I identified all sources of uncertainty affecting the value of the measurement, and I have classified the important sources of uncertainty in type A and B. These were quantified and then I prepared the budget of uncertainty

Keywords : uncertainty, water, total phosphorus, budget, laboratory.

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Evaluation of the Uncertainty of Measurement

For Determination of Total Phosphorus in Water by Means of Merck 1.14848

Valcan Angela

Abstract - This paper presents the calculation of uncertainty of measurement to determine total phosphorus in water by spectrophotometric method. For evaluation of uncertainty I identified all sources of uncertainty affecting the value of the measurement, and I have classified the important sources of uncertainty in type A and B. These were quantified and then I prepared the budget of uncertainty.

Keywords : uncertainty, water, total phosphorus, budget, laboratory.

I. PRINCIPLE

Phosphate ions in solution acidified with sulfuric acid reacts with molybdate ions to form molybdophosphoric acid is reduced by ascorbic acid phosphomolybdic blue (PMB) which is determined photometrically at 690 nm.

II. DEFINITIONS

a) Uncertainty of Measurement

Parameter, associated with a test result which characterizes the dispersion of values that could reasonably be attributed to the measurement.

b) Uncertainty Budget

A table which centralizes the size to which uncertainty is associated, the value / estimate size, standard uncertainty, probability distributions, coefficient sensitivity, contributing to uncertainty / relative standard uncertainty (ratio of standard uncertainty and sensitivity coefficient)

c) Assessment of type A (uncertainty)

Method for analyzing the uncertainty by the statistical analysis of the sequence of observations.

d) Assessment of type B (uncertainty)

Method of evaluating the uncertainty by means other than statistical analysis of the sequence of observations.

e) Standard Uncertainty

Uncertainty about the outcome of a measurement expressed as standard deviation.

f) Combined standard uncertainty, u_c

Standard uncertainty of the result of a measurement when that result is obtained based on the values of different sizes, equal to the positive square root of a sum of terms, those terms being the variances or covariances of those sizes, weighted in accordance with variation of the measurement for varying respective sizes.

g) Expanded Uncertainty, U

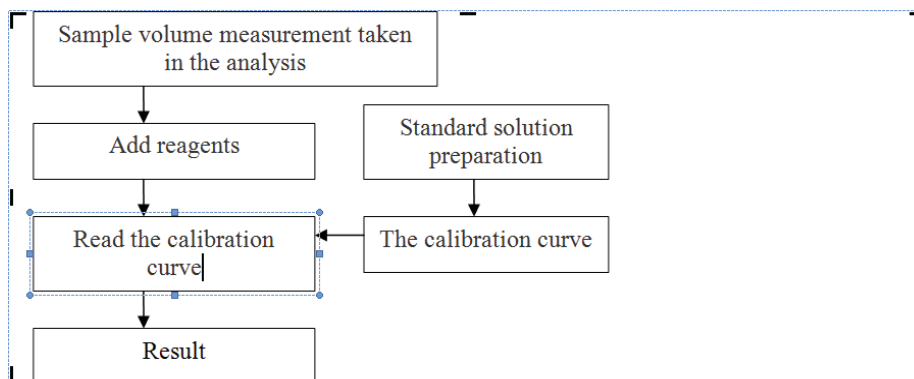
Quantity defining an interval around a measurement result, the range is expected to be within a fraction of the distribution of high values that can reasonably be attributed to the measurement.

h) Coverage Factor, K

Numerical coefficient used as a multiplier of the combined standard uncertainty to obtain the expanded uncertainty.

$U=2 \cdot u_c$, $k=2$ defines a confidence interval of approximately 95%.

III. STEP OF THE DETERMINATION OF PHOSPHORUS

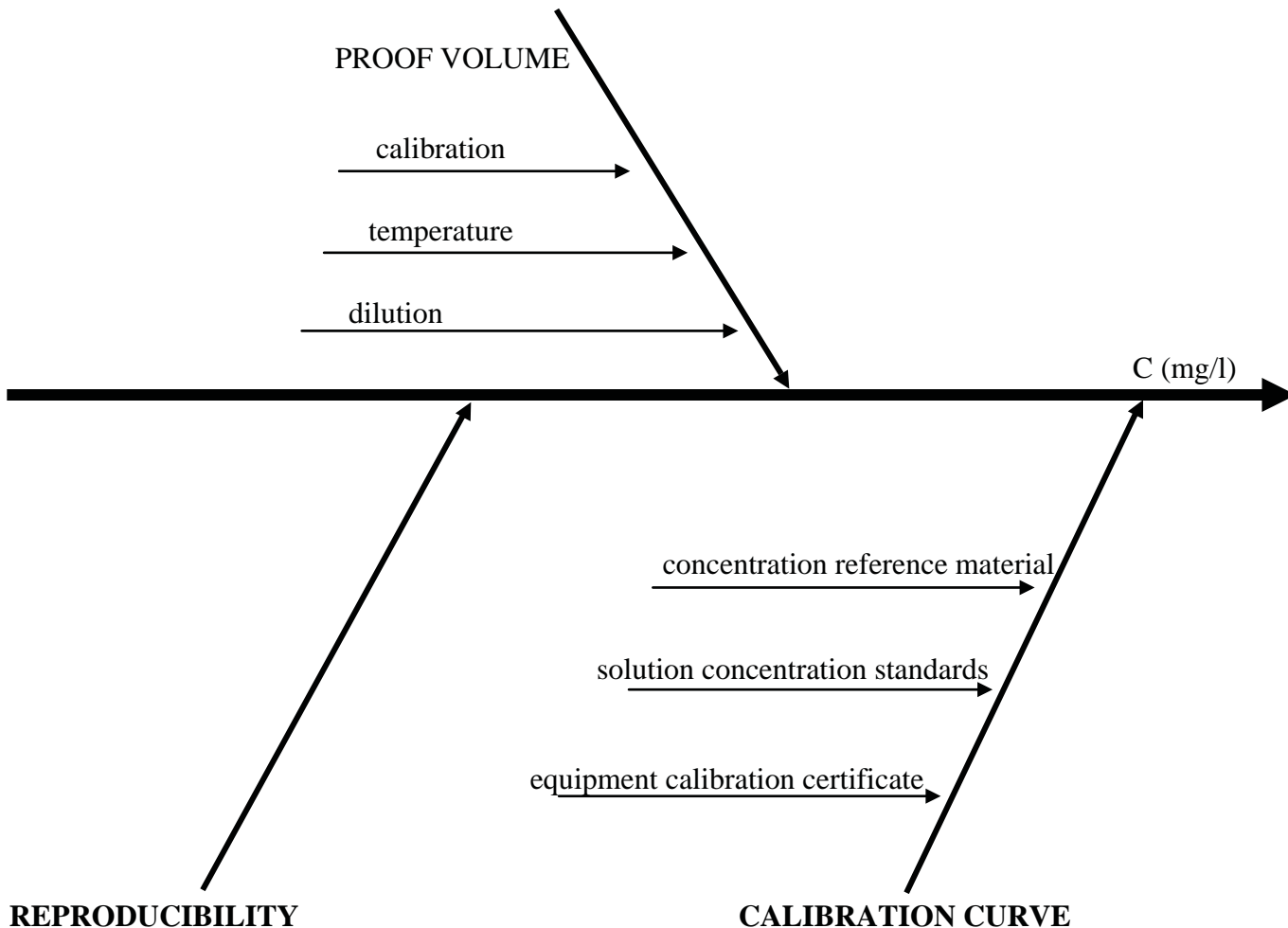


IV. IDENTIFY SOURCES OF UNCERTAINTY

To identify sources of uncertainty:

- all the sources of uncertainty affecting the value of measurement are listed;
- sources of uncertainty that have been found unimportant, will be deleted;
- the diagram cause and effect is constructed (diagram Ishikawa).

CAUSE-AND-EFFECT DIAGRAM



REPRODUCIBILITY

WITHIN-LABORATORY

Sources of uncertainty within-laboratory analyzes concerned the diagram – effect (of all sizes that affect the result). Also included are important sources of type A and B.

V. QUANTIFICATION OF UNCERTAINTIES

Uncertainties are evaluated by the method of type A and type B.

a) *Sample volume (dilution)*

Measure the sample volume using a 5 ml pipette, class A, with a tolerance of $\pm 0,03$.

i. *Glass calibration*

a- measurement tolerance;

$$u_{\text{etal.}} = \frac{a}{\sqrt{6}} = \frac{0,03}{\sqrt{6}} = 0,0122\text{ml}$$

ii. *Repeatability*

10 are measurements of volume are made, then the average is calculated, and then the standard deviation, which is

$$u_{\text{repet.}} = 0,029 \text{ ml}$$

iii. *Temperature*

$$u_{\text{temp.}} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{5 \cdot 4 \cdot 2,1 \cdot 10^{-4}}{\sqrt{3}} = 0,0024\text{ml}$$

Where: V-volume

ΔT -temperature interval

α -thermal expansion coefficient for water: $2,1 \cdot 10^{-4} \text{K}^{-1}$

$$u_v = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0,0316ml$$

Calculation of the relative uncertainty ($u_{proof\ vol.}$):

$$u_{proof\ vol} = \frac{0,0316ml}{5ml} = 0,0063$$

b) *The calibration curve*

Uncertainty of the calibration is obtained by composing the uncertainty of the measuring equipment (spectrophotometer), the reference material, the preparation of working standard solutions and standard deviation S_{x_0} calculated according to the standard method ISO 8466-1/1999.

i. *Equipment calibration certificate*

Certificate of calibration of the spectrophotometer no. 05.01-056/2011:

Expanded uncertainty: $U = 0,012$ for $k = 2$ and $P = 95\%$ at 690 nm

Uncertainty consists: $u_c = \frac{U}{k} = \frac{0,012}{2} = 0,006$

Relative uncertainty ($u_{calibration\ certif.}$):

$$u_{calib.certif.} = 0,006$$

ii. *The calibration curve no. 8/2013 was evaluated according to ISO 8466.*

We chose to work from 0,05 to 3,65 mg/l PO_4 -P wastewater, 10 points were selected for different levels, balanced on the chosen work.

The first and last points of concentration were made for 10 determinations, accounting for 10 values of pads for each point. Values were plotted according to the strength pads. The method proved linear chosen field by performing verification tests: homogeneous dispersion and linearity.

a. *Solutions for calibration curve preparation*

Out of the reference material Merck KH_2PO_4 in H_2O , 999 ± 2 mg/l standard solution I was prepared and work of 10 mg/l and standard working solution II 1 mg/l.

i. *Reference material*

$$u_{MR.} = \frac{a}{\sqrt{3}} = \frac{2}{\sqrt{3}} = 1,1547mg/l$$

Calculation of the relative uncertainty ($u_{conc.MR.}$):

$$u_{conc.MR} = \frac{1,1547mg/l}{999mg/l} = 0,0012$$

ii. *Standard solution I of concentration 10 mgP/l:*

Take 7, 68 ml of Merck standard solution with a burette of 10 ml and placed in a 250 ml volumetric flask and dilute to the mark with distilled water.

a. *burette 10 ml (class A, 0,02 ml mark, tolerance $\pm 0,02$ ml)*

1. *Glass calibration*

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0,02}{\sqrt{6}} = 0,0082ml$$

2. *Repeatability are 10 measurements of volume averaging, standard deviation which is*

$$u_{repet.} = 0,005\ ml$$

3. *Temperature*

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{7,68 \cdot 4 \cdot 2,1 \cdot 10^{-4}}{\sqrt{3}} = 0,0037ml$$

$$u_{burette} = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0,0103ml$$

Calculation of the relative uncertainty ($u_{burette}$):

$$u_{V_{burette}} = \frac{0,0103ml}{8,6\ ml} = 0,0013$$

b. *250 ml volumetric flask (class A tolerance of $\pm 0,15$ ml)*

1. *Glass calibration*

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0,15}{\sqrt{6}} = 0,0612ml$$

2. *Repeatability are 10 measurements of volume averaging, standard deviation which is*

$$u_{repet.} = 0,092\ ml$$

3. *Temperature*

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{250 \cdot 4 \cdot 2,1 \cdot 10^{-4}}{\sqrt{3}} = 0,1212ml$$

$$u_{balloon250} = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0,164ml$$

Calculation of the relative uncertainty ($u_{balloon\ 250}$):

$$u_{V_{balloon\ 250}} = \frac{0,164ml}{250ml} = 0,00066$$

Calculation of the relative uncertainty ($u_{sol.et.I.}$):

$$u_{V_{sol.et.I.}} = \sqrt{u_{MR}^2 + u_{V_{burette}}^2 + u_{V_{balloon}}^2} = 0,0019$$

iii. *Standard solution II of concentration 1 mgP/l:*

10 ml of standard working solution I is taken with a 10 ml burette (Class A, 0,02 ml mark, tolerance \pm

0,02 ml) and it is placed in a flask of 100 ml and then make up to volume with distilled water.

a. burette 10 ml (Class A, 0,02 ml mark, tolerance ± 0,02 ml)

1. Glass calibration

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0,02}{\sqrt{6}} = 0,0082ml$$

2. Repeatability - 10 volume measurements are made, their average and the standard deviation which is

$$u_{repet.} = 0,005 ml$$

3. Temperature

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{10 \cdot 4 \cdot 2,1 \cdot 10^{-4}}{\sqrt{3}} = 0,0485ml$$

$$u_{burette} = \sqrt{u_{etal.}^2 + u_{repet.}^2 + u_{temp.}^2} = 0,01073ml$$

Calculation of the relative uncertainty ($u_{burette}$):

$$u_{V_{burette}} = \frac{0,01073ml}{10ml} = 0,001073$$

b. 100 ml volumetric flask (class A tolerance of ± 0.01 ml)

1. Glass calibration

$$u_{etal.} = \frac{a}{\sqrt{6}} = \frac{0,01}{\sqrt{6}} = 0,0041ml$$

$$u_{reading\ the\ curve} = \sqrt{u_{certif.etal.}^2 + u_{Sx0}^2 + u_{sol.et.I}^2 + u_{sol.et.II}^2} = 0,0120$$

c) Within-laboratory reproducibility

Concentrations were taken from the control chart (98 values determined in the period 3 January 2012-31 March 2013) and were calculated:

i. Arithmetic mean: ratio of sum of x_i and their number, n .

$$\bar{x} = \frac{\sum x_i}{n} = 1,496mg/l, n=98$$

ii. standard deviation S :

$$S = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} = 0,0137mg/l$$

Where:

x_i - outcome measurement (values corresponding to n measurements)

\bar{x} – arithmetic mean of n data

2. Repeatability – 10 volume measurements are made, then their average and the standard deviation which is

$$u_{repet.} = 0,090 ml$$

3. Temperature

$$u_{temp.} = \frac{V \cdot \Delta T \cdot \alpha}{\sqrt{3}} = \frac{100 \cdot 4 \cdot 2,1 \cdot 10^{-4}}{\sqrt{3}} = 0,0485ml$$

Calculation of the relative uncertainty ($u_{balon\ 100}$):

$$u_{V_{balloon100}} = \frac{0,1023ml}{100ml} = 0,001023$$

Calculation of the relative uncertainty ($u_{sol.et.II}$):

$$u_{V_{sol.et.II}} = \sqrt{u_{sol.et.I}^2 + u_{V_{burette}}^2 + u_{V_{balloon}}^2} = 0,00240$$

b. Following the evaluation of the calibration no.8/2013, the ISO 8466 standards were obtained:

- standard deviation of the method $S_{x_0} = 0,0185 mg/l$.
- average concentrations of standard solutions of curve $x_0 = 1,85 mg/l$

Calculation of the relative uncertainty (u_{Sx_0}):

$$u_{S_{x_0}} = \frac{0,0185mg/l}{1,85mg/l} = 0,010$$

$n-1$: degrees of freedom

i – number of measurements (43)

iii. Relative standard deviation: n values measured for the calculation equation is:

$$RSD = \frac{S}{\bar{x}} = \frac{0,0137}{1,496} = 0,0091$$

Standard uncertainty evaluated as type method can be:

$$u_{xi} = RSD = 0,0091$$

d) Bias

Analyzing samples of known concentration (reference material) and comparing the measured value with the real one.

$$u_{bias} = \frac{|x_{ref} - \bar{x}|}{x_{ref}} = \frac{1,500 - 1,496}{1,500} = 0,0026$$

VI. UNCERTAINTY BUDGET

	Method of evaluation	Value (x) UM	Standard uncertainty u(x)	Relative standard uncertainty u(x)/x
Proof volume	Type B (glassware)	5 ml	0,0316 ml	0,0063
The calibration curve				
a. certificate calibration equipment	Type B			0,006
b. standard working solution I	Type A			0,0019
c. standard working solution II	Type A			0,0024
d. evaluation of the calibration curve	Type A	1,85 mg/l	0,0185	0,010
Within-laboratory reproducibility	Type A	1,496 mg/l	0,0137	0,0091
Bias	Type A	1,5 mg/l		0,0026

COMPOSITE UNCERTAINTY OF THE PROCEDURE IS:

$$u_c = \sqrt{u_{\text{proof vol.}}^2 + u_{\text{reading the curve}}^2 + u_{x_i}^2 + u_{\text{bias}}^2} = 0,0166$$

THE EXPANDED UNCERTAINTY is calculated from the combined standard uncertainty multiplied by a coverage coefficient, k.

$$U = k \cdot u_c$$

choice of k is based on a level of confidence required.

Expanded uncertainty at confidence level 95%, k=2 is U=0,033; 3, 31%.

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Synthesis, Characterization and Biological Activities of Cu(II), Ni(II), Zn(II), Cd(II), Sn(II), Co(II), Sb(III) and Fe(III) Complexes with Schiff base Methyl 3-[(E,E)-3-phenylprop-2-enylidene] dithiocarbazate

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Abstract - The Complexes of Cu(II), Ni(II), Zn(II), Cd(II), Sn(II), Co(II), Sb(III) and Fe(III) with Methyl 3-[(E,E)-3-phenylprop-2-enylidene]dithiocarbazate have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, FT-IR, UV-Visible spectroscopy. The Schiff bases in every case behaved as bidentate, uninegative ligands. The complexes of Cu(II), Co(II) and Fe(III) are paramagnetic while all other complexes are diamagnetic. The complexes $[\text{Cu}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ and $[\text{Ni}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ had, square planar structures with two ligands satisfying the four stereochemical sites, where the complexes $[\text{Zn}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ and $[\text{Cd}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ were tetrahedral and the complexes $[\text{Sn}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{H}_2\text{O})_2]$, $[\text{Co}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{H}_2\text{O})_2]$, $[\text{Sb}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$ and $[\text{Fe}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$ were octahedral in geometry. The metal complexes have been screened for their antibacterial activity.

Keywords : metal complexes; antimicrobial; ir spectra; uv-vis spectra.

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Synthesis, Characterization and Biological Activities of Cu(II), Ni(II), Zn(II), Cd(II), Sn(II), Co(II), Sb(III) and Fe(III) Complexes with Schiff base Methyl 3-[(E,E)-3-phenylprop-2-enylidene]dithiocarbazate

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Abstract - The Complexes of Cu(II), Ni(II), Zn(II), Cd(II), Sn(II), Co(II), Sb(III) and Fe(III) with Methyl 3-[(E,E)-3-phenylprop-2-enylidene]dithiocarbazate have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, FT-IR, UV-Visible spectroscopy. The Schiff bases in every case behaved as bidentate, uninegative ligands. The complexes of Cu(II), Co(II) and Fe(III) are paramagnetic while all other complexes are diamagnetic. The complexes $[\text{Cu}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ and $[\text{Ni}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ had, square planar structures with two ligands satisfying the four stereochemical sites, where the complexes $[\text{Zn}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ and $[\text{Cd}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ were tetrahedral and the complexes $[\text{Sn}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{H}_2\text{O})_2]$, $[\text{Co}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{H}_2\text{O})_2]$, $[\text{Sb}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$ and $[\text{Fe}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$ were octahedral in geometry. The metal complexes have been screened for their antibacterial activity.

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I. INTRODUCTION

Chemistry of nitrogen-sulfur donor ligands and their complexes had been of interests for their interesting coordination chemistry and also for their profound biomedical properties. Dithiocarbazate, $\text{NH}_2\text{NHCS}_2^-$ and its substituted derivatives have been synthesized and investigated over the past few decades [1-28]. Dithiocarbazic acid and the Schiff base derived from its S-alkyl and S-benzyl esters form an interesting series of ligands and metal complexes. Researchers in this area have been continuing the synthesis of new nitrogen-sulphur donor ligands through Schiff base condensation with aldehyde and ketones. The properties of these ligands can be greatly modified through the introduction of organic substituents. The number of ligands synthesized continues to increase because of the intriguing observation that different ligands show different biological properties, although they may differ only slightly in their molecular structures [1-11, 15-22].

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Transition metal complexes of these ligands are also widely studied because of their potential for therapeutic use [2-4,6-20]. For example the Schiff base of 2-benzoylpyridine with S-methyl dithiocarbazate (HBP-SMe) inhibits the growth of bacteria, E. coli and S. aureus to some extent while that with S-benzyl dithiocarbazate (HBP-SBz) shows no effect at all on the two mentioned bacteria[22]. To date, no pattern has emerged to enable the activity to be predicted on the basis of structure or substituents. Reports on the bioactivities of the starting ligands, S-methyl dithiocarbazate (SMDTC) and Schiff bases have not yet been widely studied. The mode of interaction of these compounds with the cancer cells and microbes are yet to be investigated. In order to study the influence of metal ions and substituents on the structure and biological activity and as part of our continuing work on metal-Schiff base, we report here the synthesis, structure and bioactivity of complexes of a nitrogen-sulfur chelating agent derived from Cinnamaldehyde Schiff base of S-methyldithiocarbazate (SMDTC).

a) Related Literature

There had been immense interests in nitrogen-sulfur donor ligands of S-methyldithiocarbazates (SMDTC) due to their biomedical, electrooptical and catalytic properties. A number of Schiff bases and derived from SMDTC and their metal complexes have been reported [29-43]. For the synthesis and structure of zinc complexes of S-methyldithiocarbazates [29-30]. For the crystal structure of zinc complex of SBDC [31]. For the synthesis and structure of other metal complex of SMDTC [32-39]. For the bioactivity of zinc complex of SMDTC Schiff base [29]. For the bioactivity of other metal complexes of SMDTC [34, 37, 40] For the non-linear optical property of metal complex of SMDTC [41]. For the metal induced cyclization of SMDTC Schiff bases [39]. For the photochemical reactivity of metal complex of SMDTC [41]. For the cinnamaldehyde Schiff base of SBDC and Zn(II) complex [42-43].

II. MATERIALS AND METHODS

a) Materials

Reagent grade chemicals were used without further purification in all the synthetic work. All solvents were purified by standard methods. Metal salt, cinnamaldehyde, other chemicals were obtained from Baker and used as received. Ethanol, Methanol, Acetone, Acetonitrile, DMSO and DMF were used as solvents purchased from Merck and Loba chemicals.

b) Experimental

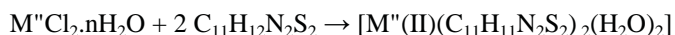
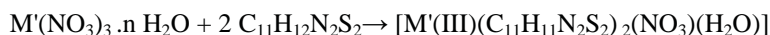
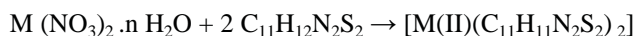
The weighing operation was performed on a METTER TELEDIO AB 204 electronic balance. Melting points of the complexes were obtained with an electrothermal melting point apparatus model No. A. Z 6512. Infrared spectra were recorded as KBr with a SHIMADZU FTIR-8101 infrared spectrophotometer, from 4000-350 cm^{-1} in the Sylhet Shahjalal University of Science and technology, Sylhet. Electrical conductivity measurements of the complexes were recorded at room temperature (25°C) for 10^{-3} M solutions of the sample in DMSO using a type CG 857 No. 71798 SCHOTT-GERATE GmbH, Germany, digital conductivity meter. Magnetic susceptibilities were measured at 25°C by the Gouy method using SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance. Diamagnetic corrections were estimated from Pascal's constant. The magnetic

moments were calculated from the equation:

$\mu_{\text{eff}} = 2.84 \sqrt{\chi_m^{\text{corr}} \times T}$. Electronic spectra of the metal complexes were obtained in Nujol mulls using a Shimadzu UV-240 UV-Vis recording spectrometer. The biological activity of the complexes were studying microbial laboratory of Department of Pharmacy, University of Rajshahi.

c) Synthesis of the metal complexes

The Schiff base, $[\text{C}_6\text{H}_5\text{-CH=CH-CH=N-NH-C(S)-SCH}_3]$, was derived from the condensation of cinnamaldehyde with S-methyldithiocarbamate was previously reported [44]. Metal salt with hydrate $\{[\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}] (0.241 \text{ g}, 1 \text{ mmol}); [\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}] (0.290 \text{ g}, 1 \text{ mmol}); [\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}] (0.297 \text{ g}, 1 \text{ mmol}); [\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}] (0.308 \text{ g}, 1 \text{ mmol}); [\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}] (0.225 \text{ g}, 1 \text{ mmol}); [\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}] (0.238 \text{ g}, 1 \text{ mmol}); [\text{Sb}(\text{NO}_3)_3] (0.306 \text{ g}, 1 \text{ mmol}) \text{ and } [\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}] (0.404 \text{ g}, 1 \text{ mmol})\}$ was dissolved in absolute ethanol (15 ml). The Schiff base (M.W 236.35) (0.472 g, 2 mmol) in hot absolute ethanol (50 ml) was added to the metal solution. The mixture was then refluxed for 30 mins and then cooled. The precipitate was filtered off and washed with hot ethanol and dried in *vacuo* over anhydrous CaCl_2 .



Where,

M = Cu(II), Ni(II), Zn(II) and Cd (II).

M' = Sb(III) and Fe(III).

M'' = Sn(II) and Co(II).

$\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}_2$ = Cinnamaldehyde Schiff base of SMDTC

III. RESULT AND DISCUSSION

a) Physical Properties and Molar Conductance

Physical properties of the complexes were given in Table-1. The analytical data were in good agreement

with the proposed empirical formula of the present complexes.

Table 1 : Analytical data and physical properties of the complexes

Complexes	F.W.	Colour	Melting point (°C)	Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Elementary analysis, found/(Calc)%				
					C	H	N	S	M
SMDTC	122.13	White	81	2.30					
$[\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}_2]$	236.35	Orange	170	2.10	55.76 (55.90)	5.05 (5.12)	11.67 (11.85)	27.00 (27.13)	-
$[\text{Cu}(\text{II})(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$	534.21	Greenish brown	188	3.25	49.44 (49.46)	4.22 (4.15)	10.36 (10.49)	23.79 (24.01)	11.40 (11.89)

[Ni(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	529.35	Golden brown	268	1.90	49.60 (49.91)	4.11 (4.19)	10.78 (10.58)	23.88 (24.23)	10.78 (11.09)
[Zn(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	536.05	Light yellow	205	3.10	49.35 (49.29)	4.07 (4.14)	10.32 (10.45)	24.00 (23.93)	11.80 (12.20)
[Cd(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	583.07	Yellow	208	2.15	45.20 (45.32)	3.65 (3.80)	9.52 (9.61)	21.63 (21.99)	19.15 (19.28)
[Sn(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (H ₂ O) ₂]	625.37	Reddish yellow	210	2.05	42.00 (42.25)	4.00 (4.19)	9.00 (8.96)	20.33 (20.51)	18.56 (18.98)
[Co(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (H ₂ O) ₂]	565.61	Reddish black	220	2.50	47.00 (46.72)	4.56 (4.63)	9.56 (9.91)	22.56 (22.68)	10.22 (10.41)
[Sb(III)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	672.42	Cream	190	2.35	39.47 (39.30)	3.80 (3.60)	10.78 (10.90)	18.87 (19.07)	17.67 (18.11)
[Fe(III)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	606.61	Black	198	2.56	43.38 (43.56)	3.80 (3.99)	11.33 (11.54)	21.00 (21.14)	8.86 (9.21)

The conductance values of the prepared complexes were illustrated in Table-1. The conductance values of the complexes reveal that these were non electrolyte in nature [45].

b) IR Studies

SMDTC showed all the characteristic bands as reported in the literature [46]. The IR spectrum of SMDTC (Table-2) showed strong intensity bands at 3365 cm⁻¹ and 3220 cm⁻¹ which were assigned to the asymmetric $\nu(N-H)$ and symmetric $\nu(N-H)$ modes of the NH₂ group, respectively. The $\nu(C=S)$ band for SMDTC appeared at 1064 cm⁻¹.

The IR spectrum (Table:2) of the Schiff base showed strong bands at 3210 cm⁻¹. This was attributed to the secondary amine $\nu(N-H)$ mode of the free ligands. The thione groups are relatively unstable in the monomeric form and tend to turn to the more stable thiole forms by enethiolization in solution (Fig.1.1). The

absence of $\nu(S-H)$ absorbance at approximately 2570 cm⁻¹ indicates that in the solid state, the bases exist primarily in the thione form. The disappearance of $\nu(N-H)$ bands their spectra of the metal complexes suggests deprotonation and consequent co-ordination through the thiolate anions. The Schiff base also showed strong bands at ≈ 1580 cm⁻¹. These are assigned to the $\nu(C=N)$ modes for the free ligand. In the metal complexes, this stretching band shifted to lower frequencies, due to the lowering of the C=N bond order as a result of the metal-nitrogen bond formation. The Schiff base also showed $\nu(C=S)$ modes at 1055 cm⁻¹. The $\nu(C=S)$ mode observed in the free ligand disappeared in the complexes, thus supporting the above contention of thiolate bonding with metal ions. Consequently the $\nu(C-S)$ mode was observed in the spectra of the complexes supporting thiolate bindings.

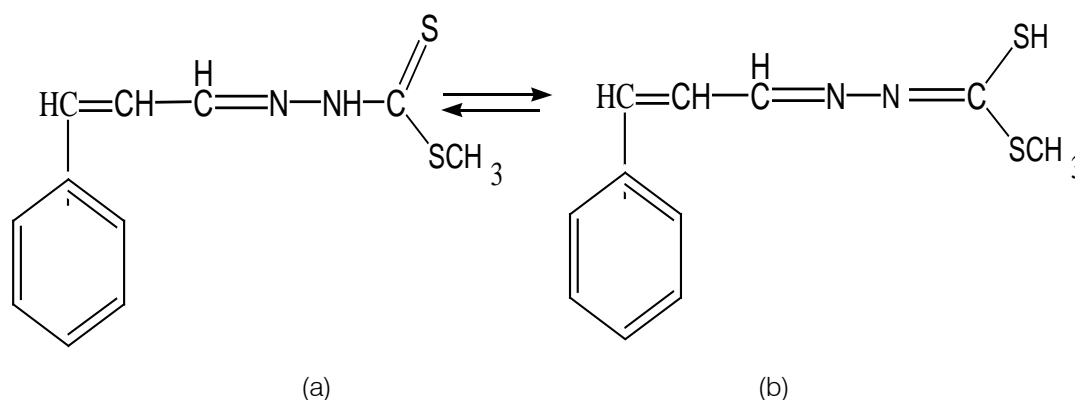


Figure 1.1 : Tautomeric forms (a) Thione form (b) Thiolo form

The C=N stretching vibration in the free NS Schiff base appeared at ≈ 1580 cm⁻¹, which upon complexation, shifted towards lower frequency regions, at ≈ 1530 cm⁻¹ (Table:2). This lowering of C=N stretching mode on complexation supported coordination through nitrogen atom. The mode of the free Schiff base

appeared at 1055 cm⁻¹. This band also disappeared in the IR spectra of the metal complexes giving evidence of coordination through the thiolate anion. The Schiff base coordinated to the metal through the thiolate sulphur and the β -nitrogen as evident from the IR spectrum showing bands at ≈ 384 cm⁻¹ and ≈ 491 cm⁻¹, corres-

ponding to $\nu(\text{M-S})$ and $\nu(\text{M-N})$ stretching modes, respectively.

In case of complexes $[\text{Sn(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{H}_2\text{O})_2]$, the IR band at $3250\text{-}3300\text{ cm}^{-1}$ was indicated of the presence of coordinated water molecule.

IR spectra for the complexes $[\text{Sb}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$ and $[\text{Fe(III)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$ display bands at about 1480 and 1255 cm^{-1} suggesting the presence of ionic nitrate group [47]. The IR band at $3250\text{-}3300\text{ cm}^{-1}$ was indicated of the presence of coordinated water molecule.

Table 2 : Important infrared spectral bands of the ligands and metal complexes

Compounds	ν (NH ₂) cm ⁻¹	ν (N-H) cm ⁻¹	ν (C=S) cm ⁻¹	ν (C=N) cm ⁻¹	ν (C-S) cm ⁻¹	ν (M-S) cm ⁻¹	ν (M-N) cm ⁻¹	ν (OH) cm ⁻¹	ν (ON) cm ⁻¹
SMDTC	3365, 3220	3200	1064	-	-	-	-	-	-
$[\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}_2]$	-	3110	1055	1580	-	-	-	-	-
$[\text{Cu(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$	-	-	-	1535	771	384	490	-	-
$[\text{Ni(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$	-	-	-	1545	765	390	503	-	-
$[\text{Zn(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$	-	-	-	1520	750	375	495	-	-
$[\text{Cd(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$	-	-	-	1530	760	385	480	-	-
$[\text{Sn(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$	-	-	-	1550	768	410	485	-	-
$[\text{Co(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{H}_2\text{O})_2]$	-	-	-	1540	758	365	501	3300- 3250	-
$[\text{Sb(III)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$	-	-	-	1565	765	389	510	3210- 3150	1480, 1255
$[\text{Fe(III)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2(\text{NO}_3)(\text{H}_2\text{O})]$	-	-	-	1525	780	395	482	3325- 3210	1475, 1260

c) *Magnetic moment and electronic spectra*

The magnetic susceptibility measurement (Table-3) showed that the complex Cu(II) was paramagnetic. The greenish brown paramagnetic copper complex gave a magnetic moment of 1.93 B.M corresponding to one unpaired electron. The UV-vis spectrum of the complex showed d-d bands at 582 nm and 410 nm, arising from the ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions, respectively, characteristic of a square planer stereochemistry [48]. The intense band at 308 nm was presumably caused by charge transfer.

The magnetic susceptibility measurement (Table-3) showed that the complex $[\text{Ni(II)}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{S}_2)_2]$ was diamagnetic. For the electronic spectra, the diamagnetic nature of complex indicated a d-d band at ca. 440-560 nm and 600 – 800 nm. A square-planar Ni(II) configuration gives rise to three bands corresponding to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$, ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$ transitions, , but in some cases these bands were too weak or were overshadowed by other stronger absorptions in the same region[49].

The absorption bands of the Zn(II) and Cd(II) complex exhibited charge transfer M_L at 355nm and 350nm. This is because of the electronic configuration and the diamagnetic of these complexes which confirmed the absence of any d-d electronic transition [50-51]. The Zn(II) complex was distorted tetrahedral in geometry whereas Cd(II) tetrahedral.

The UV-VIS spectrum of the complex, Sb(III) and Sn (II) band at 305 nm and 302nm, arising from charge transfer transition. The magnetic susceptibility measurement showed that the complexes were diamagnetic in nature. The complexes were octahedral in geometry.

The cobalt complex Co(II) had room-temperature magnetic moments of about 3.94 B.M (Table-3) indicative of octahedral geometry. The electronic spectra of these complexes showed three bands 390, 430 and 560 nm (Table-3). This bands were assigned to the transition, ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\nu_1)$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\nu_2)$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_3)$ of octrahedral Co(II).

The electronic spectrum of the Fe(III) Complex , showed bands at 744 nm, that may be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$; indicating distorted octahedral geometry around Fe(III) ion. [52- 53] The magnetic moment of this complex was found to be 5.8 B.M. and fall within the range observed for octahedral Fe(III) complexes[54].

Table 3 : The electronic absorption spectral bands(nm) and magnetic moment(B.M) for the complexes

Complexes	$\lambda_{max}(nm)$	Band Assignment	μ_{eff} (B.M.)	Geometry
[Cu(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	308 410 582	Charge transfer $^2B_{1g} \rightarrow ^2A_{1g}$ $^2B_{1g} \rightarrow ^2E_{1g}$	1.93	Square Planar
[Ni(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	465 555 634	Charge transfer $^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1B_{1g}$	Dia	Square planar
[Zn(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	355	Charge transfer	Dia	Distorted Tetrahedral
[Cd(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	350	Charge transfer	Dia	Tetrahedral
[Sn(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (H ₂ O) ₂]	302	Charge transfer	Dia	Octrahedral
[Co(II)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (H ₂ O) ₂]	390, 430, 560	$^4T_{1g} \rightarrow ^4T_{2g}$, $^4T_{1g} \rightarrow ^4A_{2g}$, $^4T_{1g} \rightarrow ^4T_{2g}(F)$	3.94	Octahedral
[Sb(III)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	305	Charge transfer	Dia	Octahedral
[Fe(III)(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	734	$^6A_{1g} \rightarrow ^4T_{1g}(G)$	5.8	Octahedral

d) Provable Structure

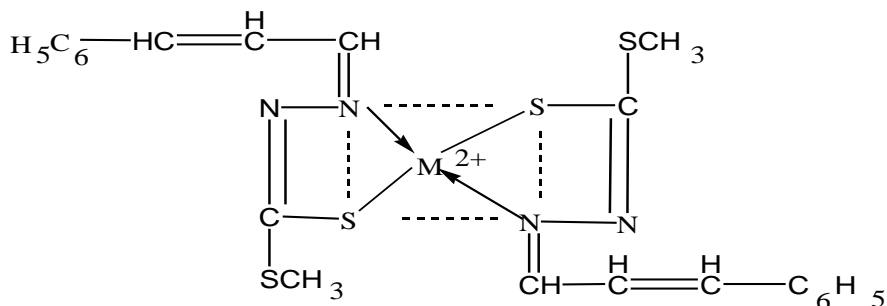


Figure 1.2 : Square planner structure of the complexes

Where, M^{2+} = Cu(II) and Ni(II)

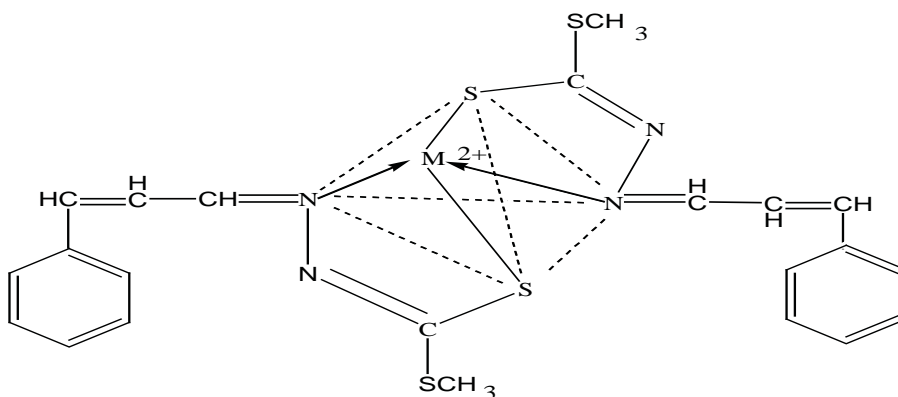


Figure 1.3 : Tetrahedral structure of the complexes

Where, M^{2+} = Zn(II) and Cd(II).

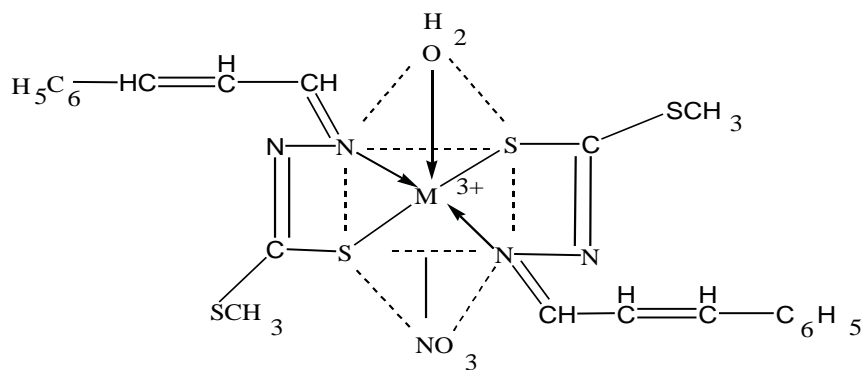


Figure 1.4 : Octahedral structure of the complexes

Where, $M^{3+} = Sb(III)$ and $Fe(III)$.

FTIR-Spectrum of Schiff base and metal complexes

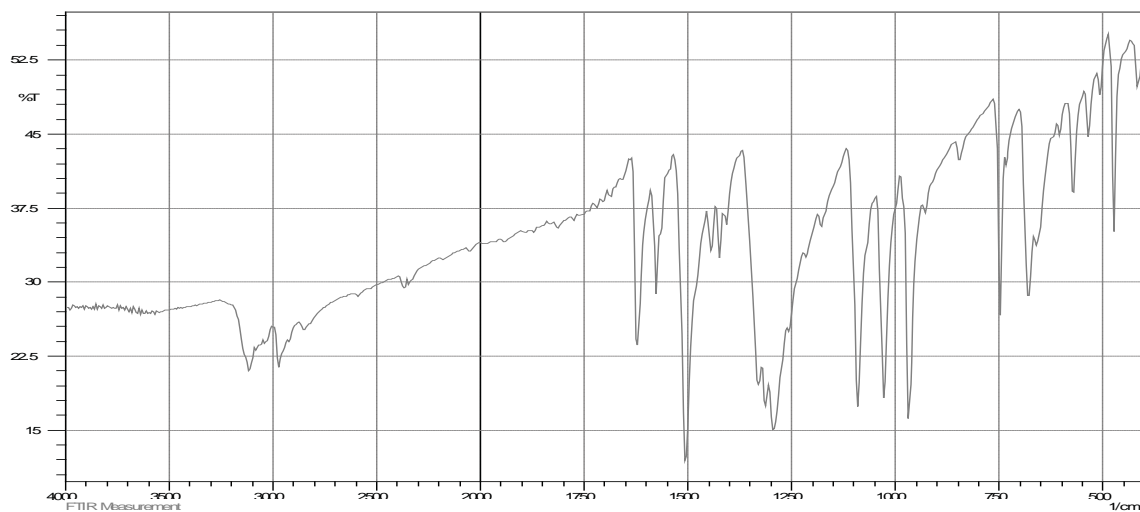


Figure 2.1 : FTIR spectrum of the cinnamaldehyde Schiff base of SMDTC($C_{11}H_{12}N_2S_2$)

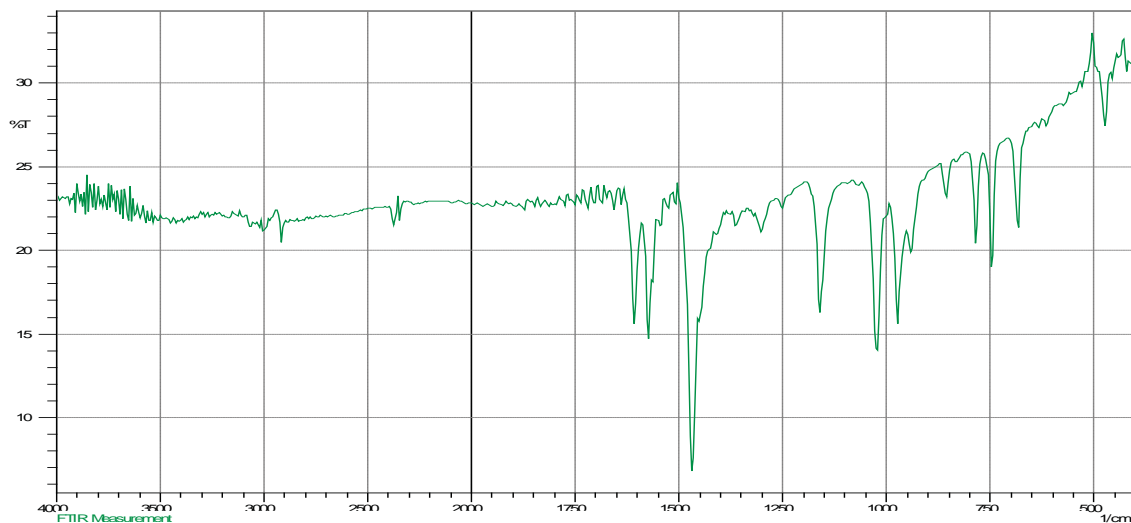


Figure 2.2 : FTIR spectrum of the complex $[Cu(II)(C_{11}H_{11}N_2S_2)_2]$

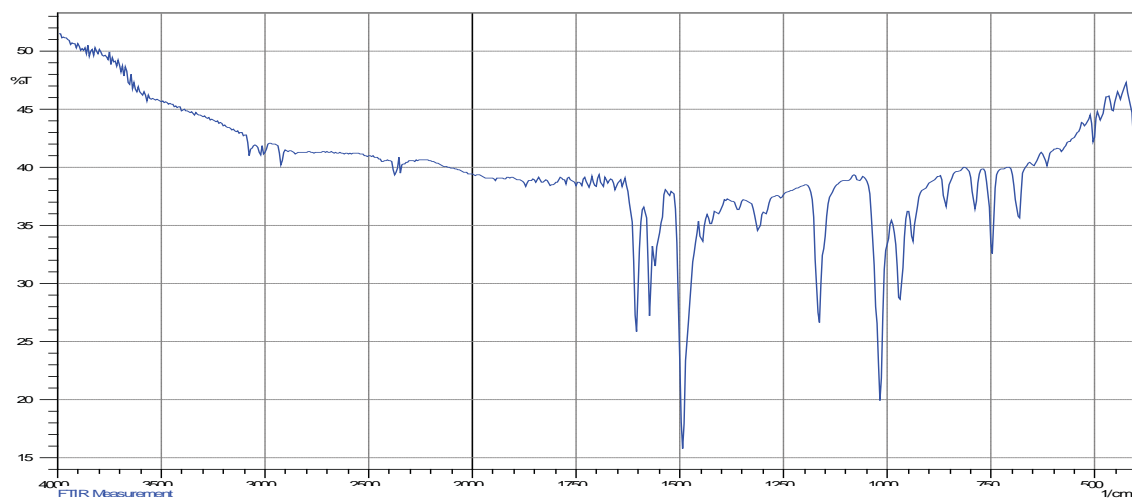


Figure 2.3 : FTIR spectrum of the complex [Ni(II)(C₁₁H₁₁N₂S₂)₂]

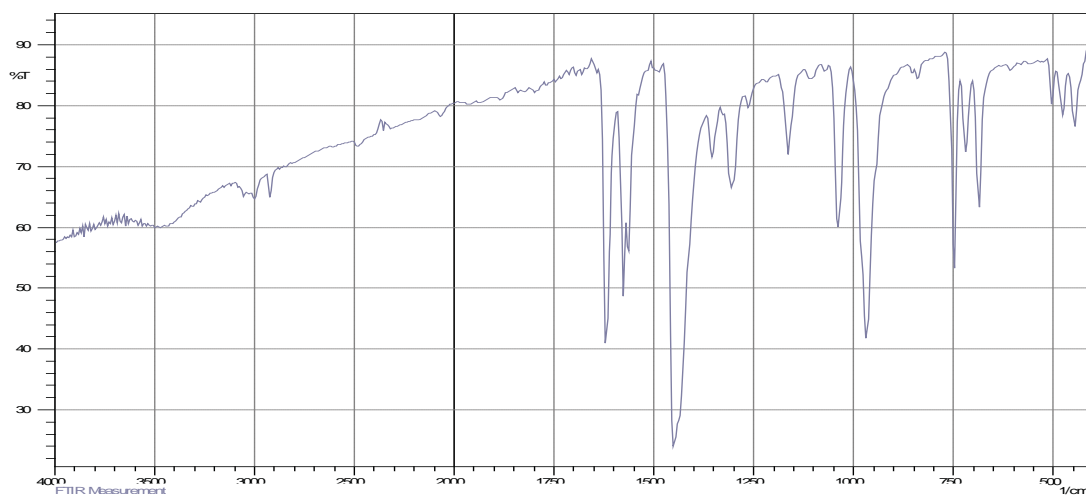


Figure 2.4 : FTIR spectrum of the complex [Zn(II)(C₁₁H₁₁N₂S₂)₂]

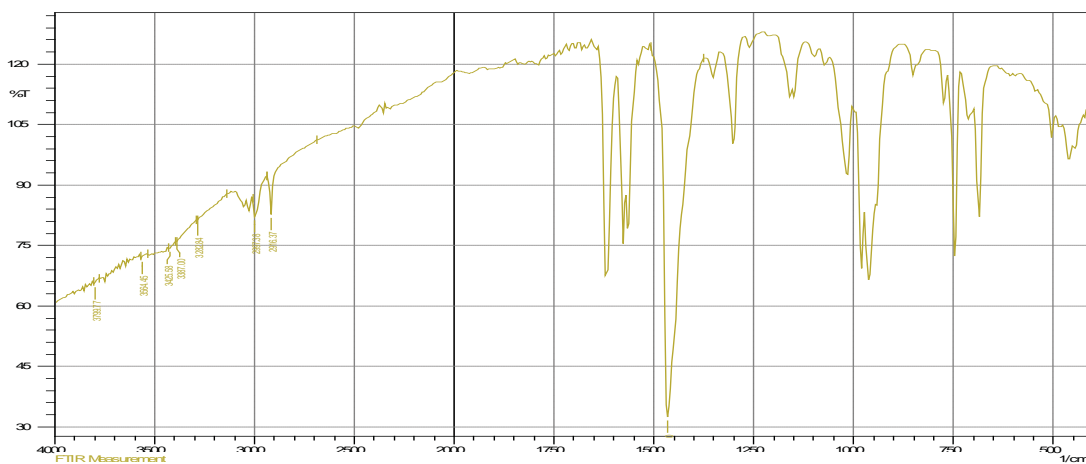


Figure 2.5 : FTIR spectrum of the complex [Cd(II)(C₁₁H₁₁N₂S₂)₂]

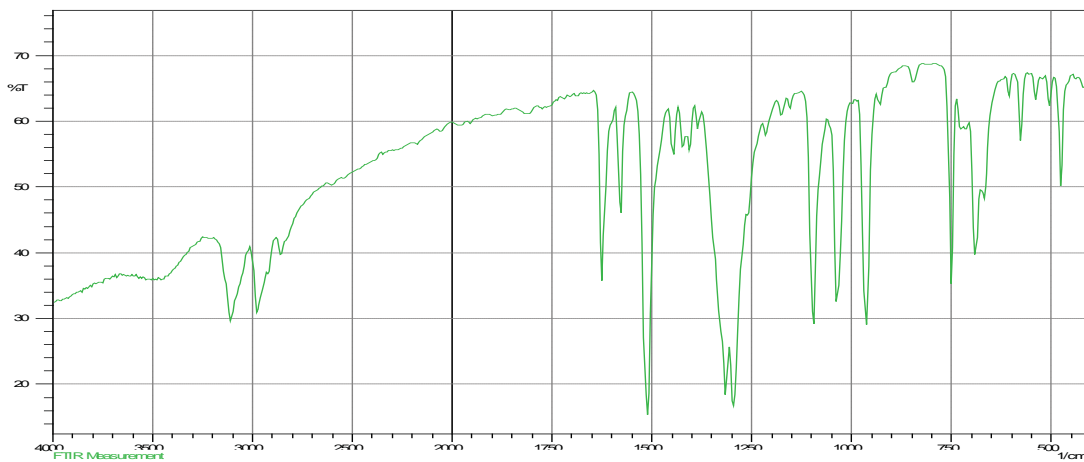


Figure 2.6 : FTIR spectrum of the complex $[Sb(III)(C_{11}H_{11}N_2S_2)_2(NO_3)(H_2O)]$

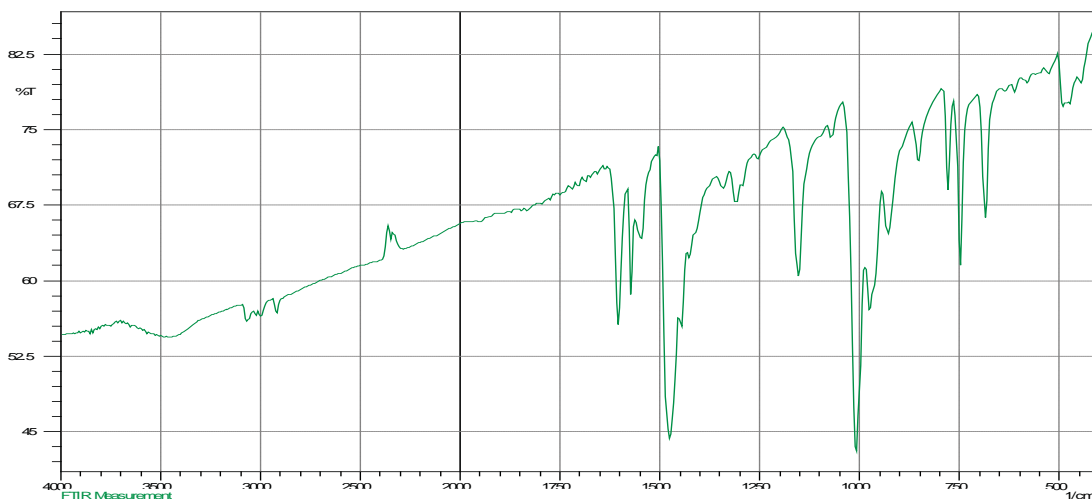


Figure 2.7 : FTIR spectrum of the complex $[Fe(III)(C_{11}H_{11}N_2S_2)_2(NO_3)(H_2O)]$

UV-Vis Spectrum of metal complexes

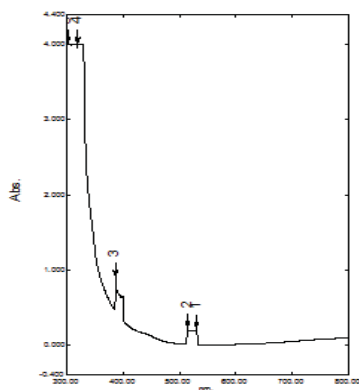


Figure 3.1 : UV-visible spectrum of the complex $[Cu(II)(C_{11}H_{11}N_2S_2)_2]$

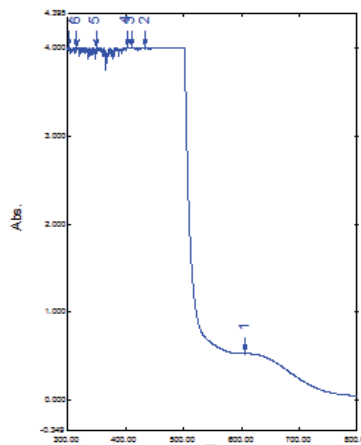


Figure 3.2 : UV-visible spectrum of the complex $[Ni(II)(C_{11}H_{11}N_2S_2)_2]$

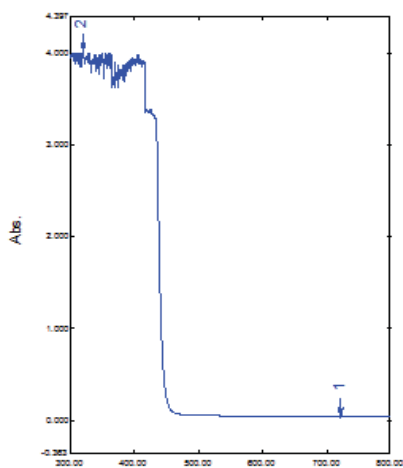


Figure 3.3 : UV-visible spectrum of the complex $[Zn(II)(C_{11}H_{11}N_2S_2)_2]$

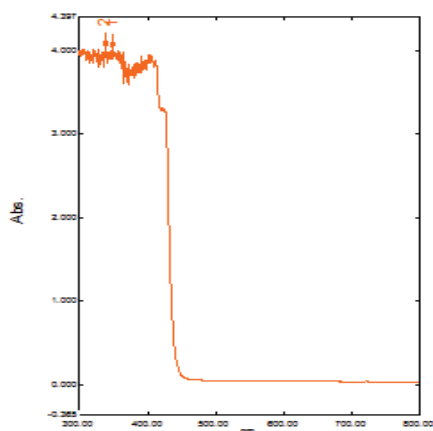


Figure 3.4 : UV-visible spectrum of the complex $[Cd(II)(C_{11}H_{11}N_2S_2)_2]$

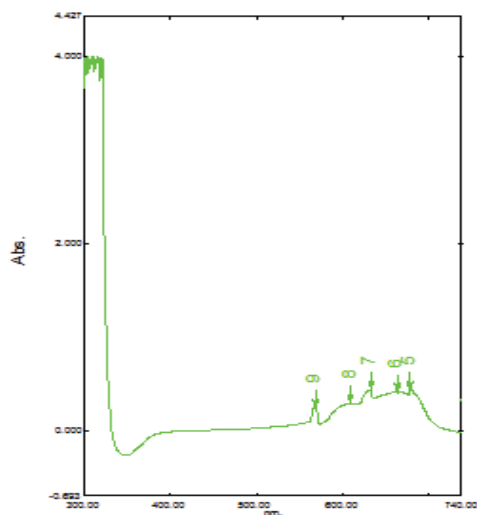


Figure 3.5 : UV-visible spectrum of the complex $[Fe(III)(C_{11}H_{11}N_2S_2)_2(NO_3)(H_2O)]$

e) *Microbial activity of the complexes*

i. *Microbial Activity*

The antibacterial activities of ligand and its metal complexes were studied by usual cup-plate agar diffusion method. The bacterial species used in the screening were *Shigella sonnei*, *Escherichia coli*, (gram negative), *Bacillus subtilis* (gram-positive). Stock cultures of the test bacterial species were maintained on Nutrient Agar media by sub culturing on petri dishes. The media were prepared by adding the components as per manufacturer's instructions and sterilized in the autoclave at 121°C temperature and 15 lbs pressure for 15 minutes and then cooled to 45-60°C. 20 mL of each medium was poured in a Petri dish and allowed to solidify. After solidification, Petri plates with media were spread with 1.0 mL of bacterial suspension, which is prepared in sterile distilled water. The wells were bored with cork borer and the agar plugs were removed. 100 µl of the compound reconstituted in $CHCl_3$ (Choloform) in concentrations of 1.0 mg/mL was added to the agar wells. The plates were incubated at 37°C for 24 hours and then the plates were observed for the growth inhibition zones. The presence of clear zones around the wells indicated that the compound is active. The diameter of the zone of inhibition was calculated in millimeters. The well diameter was deducted from the zone diameter to get the actual zone of the inhibition diameter and the values have been tabulated. Results of bactericidal screening show that the chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand (Table 4).

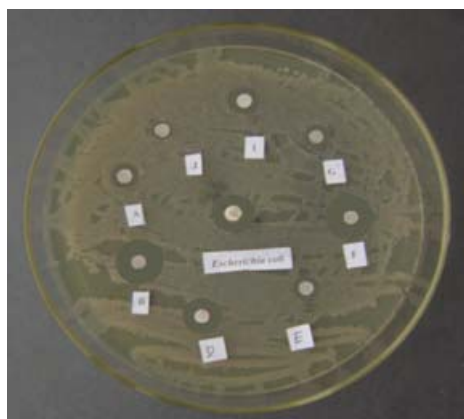
Table 4 : Antibacterial activity of the complexes with standard Kanamycin

Complexes Symbol	Compounds	Zone of inhibition, diameter in mm		
		For <i>Escherichia coli</i>	For <i>Shigella sonnei</i>	For <i>Bacillus subtilis</i>
A	[Zn(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	9	10	8
B	[Ni(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	25	24	38
C	[Cd(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	26	25	40
D	[Cu(C ₁₁ H ₁₁ N ₂ S ₂) ₂]	23	18	19
E	[Sn(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (H ₂ O) ₂]	13	14	22
F	[Co((C ₁₁ H ₁₁ N ₂ S ₂) ₂ (H ₂ O) ₂)]	13	10	16
G	[Sb(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	16	13	15
I	[Fe(C ₁₁ H ₁₁ N ₂ S ₂) ₂ (NO ₃)(H ₂ O)]	10	15	14
R	Schiff base C ₁₁ H ₁₂ N ₂ S ₂	20	19	17
	Kanamycin disc	20	20	22

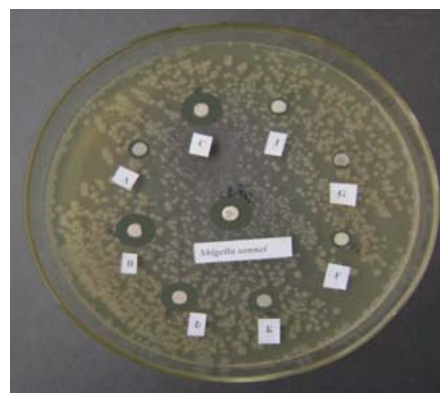
Year 2013
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Assay results refer to concentration of 100 mg/ml of samples in CHCl₃. Inhibition diameter > 20mm-strongly active.

Photographic Representation



B.1. Photographic representation of zone of Inhibition of complexes A,B,C,D,E,F,G and I against *BaCillus subtilis*



B.3 : Photographic representation of zone of inhibition of complexes A, B, C, D, E, F, G and I against *Shigella sonnei*



B.2 : Photographic representation of zone of Inhibition of complexes A,B,C,D,E,F,G and I against *Escherichia coli*

IV. CONCLUSION

All the above observations indicated that the complexes [Cu(II)(C₁₁H₁₁N₂S₂)₂] and [Ni(II)(C₁₁H₁₁N₂S₂)₂] had square planar structure with two ligands satisfying the four stereochemical sites, where the complexes [Zn(II)(C₁₁H₁₁N₂S₂)₂] and [Cd(II)(C₁₁H₁₁N₂S₂)₂] were distorted tetrahedral and tetrahedral respectively. The complexes [Sn(II)(C₁₁H₁₁N₂S₂)₂(H₂O)₂], [Co(II)(C₁₁H₁₁N₂S₂)₂(H₂O)₂], [Sb(III)(C₁₁H₁₁N₂S₂)₂(NO₃)(H₂O)] and [Fe(III)(C₁₁H₁₁N₂S₂)₂(NO₃)(H₂O)] were octahedral in geometry. The antibacterial activities of the complexes have been studied against three pathogenic bacteria two gram-negative (*Escherichia coli* and *Shigella sonnei*) and one gram-positive (*Bacillus subtilis*). In particular, Complex [Ni(C₁₁H₁₁N₂S₂)₂] and [Cd(C₁₁H₁₁N₂S₂)₂] were found to be the most effective compounds against the bacteria *Escherichia coli*. Complex [Cd(C₁₁H₁₁N₂S₂)₂] was also the most active compound against *Shigella*

sonnei where the Schiff-base was selective against the bacteria mentioned. The values have been compared with an antibacterial standard, *Kanamycin*.

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Removal of Ni, Cu and Zn from a Contaminated Soil using Different Brassica Species

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Abstract - The remediation of heavy metal (Ni, Cu and Zn) in contaminated soil by different Barley and *Brassica nigra* (IC - 247)]. Species of Barley and Brassica were grown in contaminated soil and after washing with tap water [seed was collected from Krishi Anusandhan Bhavan Pusa Delhi].

The soil were mixed different amendment [FYM, ssp, CaCO_3 and $\text{FYM}+\text{CaCO}_3$]. and metal was applied at the rate of 0 and 20 Zn +10 Cu + 2.5 Ni (mg/kg soil) in the form of hydrated salts of concerned metal viz $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. After harvesting the plant were treated with di acid and prepare sample with double distal water.

The observed concentration of Cu [2.78mg to 4.78mg], Ni [3.52mg to 6.43mg] and Zn [3.39mg to 5.5mg] respectively, in species of Rai (*B.nigra*) and observed concentration of Cu [3.95 mg to 5.49 mg], Ni [3.72 mg to 5.68 mg], Zn [4.09 mg to 5.76 mg] respectively in species of Barley.

GJSFR-B Classification : FOR Code: 050304



Strictly as per the compliance and regulations of :



Removal of Ni, Cu and Zn from a Contaminated Soil using Different Brassica Species

Sumedha Chauhan ^α & S. S. Yadav ^σ

Abstract - The remediation of heavy metal (Ni, Cu and Zn) in contaminated soil by different Barley and *Brassica nigra* (IC - 247). Species of Barley and Brassica were grown in contaminated soil and after washing with tap water [seed was collected from Krishi Anusandhan Bhavan Pusa Delhi].

The soil were mixed different amendment [FYM, ssp, CaCO₃ and FYM+CaCO₃]. and metal was applied at the rate of 0 and 20 Zn +10 Cu + 2.5 Ni (mg/kg soil) in the form of hydrated salts of concerned metal viz ZnSO₄.7H₂O, NiSO₄.6H₂O, and CuSO₄. 5H₂O. After harvesting the plant were treated with di acid and prepare sample with double distal water.

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I. INTRODUCTION

Heavy metal contamination of soil is one of the most important environmental problems throughout the world (Doumett et al, 2008; Nouri et al. 2006). The ability of heavy metals to accumulate and cause toxicity in biological system – humans, animals, Micro-organism and plants has been reported (Nouri 1980; D.amre et al. 2005). As chemical hazards heavy metals are non-biodegradable and can remain almost indefinitely in the soil environment. However, their availability to biota can change considerably depending on their chemical speciation in the soil. The adequate protraction and restoration of the soil eco-systems. Therefore, require the characterization and remediation of soil that are contaminated with heavy metals (Nouri et al. 2008; Nwachuk W. U. et al. 2010).

(Rattan et al. 2001) have reported a considerable accumulation of heavy metals like Zn, Cu, Ni and Fe in surface soil as well as vegetable and field crops grown in some villages. In effluent irrigation system, similar problems are also widely reported from other metropolises of our country (Adhikari et al. 1993).

In spite of the ever-growing number of toxic metal contaminated sites, the most commonly used method of cleaning heavy metal polluted site is

excavation and burial. But its ecological sustain inability and economic feasibility is still under interrogation. There are many chemical approaches for the decontamination of such soils. Which offers way to render the contaminates immobile. But, it will not facilitate the physical removal of the contaminates from the soil system. Meanwhile the green – cure technology of phyto – remediation offers an economically viable, socially acceptable and environmentally sound solution in contrast to those mention above.

Brissica jancea (Kumar et al. 1995; Ebbs et al. 1997) have been widely cited to be hyper accumulators for several heavy metals (Zn, Pb, Cd, Se, Ni and Cu etc.). These have also been commercial used for the purpose of phyto – remediation / removal in developed countries mainly under temperate climate (Watanabe, 1997). Different members of *Brissica* family with special reference to Indian mustard have been reported to accumulate several heavy metals in its above ground biomass.

II. MATERIALS AND METHOD

FYM (Farm Yard Manure) 36gm / pots sample, SSP (Single Super Phosphate) 1.12gm sample, CaCO₃ (calcium carbonate) 200gm / pots sample. Each sample pots were added urea and KCl 320gm / 10ml for N, for the potash KCl will be add in the form of KCl 10ml / (75gm / pots) sample pots were used to prepare a samples.

a) Apparatus

Normal laboratory, glass ware(borosilicate) a pH a multipurpose flask, AAS(atomic absorption spectrophotometer), mental heater, sample collection boatel, whatman filter paper, conical flask.

b) Processing of the soil

After collection of soil (0-15cm) from an agricultural land. The soil samples were air-dried ground and sieved to give <2mm particle size.

c) Addition of nutrients and pot filling

4kg soil was taken mixed with fertilizer solution and poured into the pot N,P,K are applied as per the set schedule for the *Brassica* crop respectively in the case of artificially contaminated soil, the dose of heavy metal added were decided based on the information collect a from literature as shown in table (1):

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Metals	Dose (mgkg ⁻¹ soil)	Source of metal in use
Ni	10 mg	NiSO ₄
Cu	40 mg	CuSO ₄ .5H ₂ O
Zn	80 mg	ZnSO ₄ .7H ₂ O

d) *Collection and processing of plant and soil samples*
Plant sample

The harvest of the different species of *Brassica* was done according to the physiological stages. The collected biomass and it was first dried in shade followed by drying in the oven at 70 °C for loss of moisture. Dry weight of both biomass and make a powder from and digestion for the determination of heavy metal content. The digestion of mixture of plant were done using a Di-acid mixture (Wear and Evans 1968) and was made up to specific volume Zn, Cu, Ni were analyzed using AAS (GBC 904 AA).

Table 2 : Physicochemical properties of experimental soil (on air dry basis)

S. N.	Properties	Naturally contaminated soil
1	pH	6.05
2	Electrical conductivity dSm ⁻¹ at 25 °C	1.89
3	Organic carbon (mg kg ⁻¹)	5.4
4	Available N (Kg ha ⁻¹)	894
5	Available P (Kg ha ⁻¹)	56
6	Available K (Kg ha ⁻¹)	1093
7	Available S (Kg ha ⁻¹)	590.4
8	C E C (Kg ⁻¹)	9.64
9	Mechanical composition	
	Sand (%)	64
	Silt (%)	14
	Clay (%)	12
10	Texture	Sandy loam
11	Total heavy metals (ppm)	

III. RESULT AND DISCUSSION

a) *Physicochemical properties of soil*

Some physic chemical properties of parent and metal spiked soil were shown in table (2).Preliminary visual inspection showed that the soil was dark brown in color indicating a low amount of humus. Textural analysis showed the preponderance sand fraction (64%) followed by silt (14%) than clay (22%) thus classifying the parent soil (soil survey the soft 1998).Sandy soil are known to have a poor retention capacity for both water and metals. The slightly acidic P^H 6.05 recorded for the parent soil is with in the rang of agricultural soil. Soil P^H plays a major function control the solubility and hydrolysis of metal hydroxides, carbonates and phosphates.

b) *Heavy metal removal from soil by different mixture of ammendments*

FYM, SSP, CaCO₃, and CaCO₃ +FYM achieve heavy metal in plant the concentration were shows in table (3). For the sample of Control ,the concentration of Cu (2.78 Mg), Ni (3.52Mg) and Zn (4.40Mg),for the sample of FYM the concentration of Cu (4.58 Mg),Ni (4.46Mg) and Zn (3.39 Mg),for the sample of SSP the concentration of Cu (3.98 Mg), Ni (4.46Mg) and Zn (5.48 Mg),for the sample of CaCO₃ the concentration of Cu (4.78 Mg), Ni (6.43Mg) and Zn (4.25Mg),for the sample of CaCO₃+FYM the concentration of Cu (3.95 Mg), Ni (3.72 Mg)and Zn (5.5 Mg) were respectively in species of *Brassica nigra* (Rai).

For the sample of control ,the concentration of Cu(5.20Mg), Ni(), and Zn(), for the sample of FYM the concentration of Cu (), Ni (),and Zn(),for the sample of SSP the concentration of Cu(), Ni() and Zn(),for the sample of CaCO₃ the concentration of Cu (), Ni() and Zn (), for the sample of CaCO₃+FYM the concentration of Cu(), Ni() and Zn () in species of *Brassica compestris* (Sarso).

Table 3 : Concentrations of heavy metals in plants

Type of sample	Species	Con. of Cu(gm)	Reference range(mg)	Con. of Ni(gm)	Reference range(mg)	Con. of Zn(gm)	Reference range(mg)
Control	Rai(<i>B.Nigra</i>)	2.78	415×10 ⁻⁵	3.52	1×10 ⁻³	4.40	8×10 ⁻³ -10 ⁻¹
FYM	Rai(<i>B.Nigra</i>)	4.58	415×10 ⁻⁵	4.46	1×10 ⁻³	3.39	8×10 ⁻³ -10 ⁻¹
SSP	Rai(<i>B.Nigra</i>)	3.98	415×10 ⁻⁵	4.46	1×10 ⁻³	5.48	8×10 ⁻³ -10 ⁻¹
CaCO ₃	Rai(<i>B.Nigra</i>)	4.78	415×10 ⁻⁵	6.43	1×10 ⁻³	4.29	8×10 ⁻³ -10 ⁻¹
CaCO ₃ +FYM	Rai(<i>B.Nigra</i>)	3.95	415×10 ⁻⁵	3.72	1×10 ⁻³	5.5	8×10 ⁻³ -10 ⁻¹
Control	Sarso(<i>B.Compestris</i>)	5.20	415×10 ⁻⁵	5.20	1×10 ⁻³	5.86	8×10 ⁻³ -10 ⁻¹
FYM	Sarso(<i>B.Compestris</i>)	4.54	415×10 ⁻⁵	4.54	1×10 ⁻³	4.06	8×10 ⁻³ -10 ⁻¹

SSP	Sarso(<i>B.Compestris</i>)	6.51	415×10^{-5}	6.52	1×10^{-3}	4.60	$8 \times 10^{-3} - 10^{-1}$
CaCo ₃	Sarso(<i>B.Compestris</i>)	6.11	415×10^{-5}	6.16	1×10^{-3}	5.47	$8 \times 10^{-3} - 10^{-1}$
CaCo ₃ +FYM	Sarso(<i>B.Compestris</i>)	3.68	415×10^{-5}	6.48	1×10^{-3}	5.86	$8 \times 10^{-3} - 10^{-1}$

III. CONCLUSION

The soil that was contaminated with Cu, Ni and Zn in was treated with FYM, SSP, CaCo₃, and CaCo₃+FYM, KCl and urea in Brassica species. The observed concentrations of Cu, Ni and Zn were 4.014 gm, 4.518 gm and 4.612 gm in *Brassica nigra* (rai) and observed concentrations of Cu, Ni and Zn were 5.208 gm, 5.78 gm and 5.17 gm in *Brassica compestris*_(sarso), respectively. By the use of this technology, we can remove heavy metals (Cu, Ni and Zn) from the contaminated soil. The green – cure technology of phytoremediation offers an economically viable, socially acceptable and environmentally sound solution.

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Kinetics of Nonbranched-Chain Processes of the Free-Radical Addition with Reactions, in Which the 1:1 Adduct Radicals Compete for Interaction with Saturated and Unsaturated Components of the Binary Reaction System

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Keywords : low-reactive radical, autoinhibitor, competition, energy, hydrogen.

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Keywords : low-reactive radical, autoinhibitor, competition, energy, hydrogen.

1. INTRODUCTION

In a binary system consisting of a saturated component and an unsaturated one, the abstraction of the most labile atom from a saturated molecule by some initiator converts this molecule into a saturated free radical (addend) capable of adding to the double bond of an unsaturated molecule to yield a saturated 1:1 adduct radical. At a sufficiently high concentration of the unsaturated component in the system, this primary adduct radical can add to another unsaturated molecule under certain conditions to yield a secondary, 1:2 adduct radical, and so on, resulting in telomerization.

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Under other conditions and at other relative reactivities of the components, the concentration of the saturated component can exceed the concentration of the unsaturated component so greatly that the most likely reaction for the primary adduct radical will be the abstraction of the least strongly bonded atom from a saturated molecule rather than addition. This reaction will yield a 1:1 adduct molecule as the ultimate product (it proceeds *via* a nonbranched-chain mechanism since it regenerates the saturated free radical carrying the chain). This reaction may compete with the parallel reaction between the 1:1 adduct radical and an unsaturated molecule. Even at a low concentration of the unsaturated component, this parallel reaction can proceed more efficiently owing to the formation, from the unsaturated molecule, of a free radical stabilized by the delocalization of the unpaired *p*-electron over, e.g., a system of conjugate bonds. This comparatively nonreactive radical does not participate in further chain propagation and inhibits the chain process, being consumed through reactions with the same radical and with the saturated addend radical. If the adduct radical abstracts some labile atom from an unsaturated molecule, it will again turn into the 1:1 adduct molecule, this time *via* a nonchain mechanism. The 1:1 adduct radical (which is the heaviest and the largest among the free radicals that result from the addition of one addend radical to the double bond of the molecule) may have an increased energy owing to the energy liberated in the transformation of a C=O, C=C, or O=O double bond into an ordinary bond (30–130 kJ mol⁻¹ for the gas phase under standard conditions [1–4]). Therefore, it can decompose or react with one of the surrounding molecules in the place of its formation without diffusing in the solution and, hence, without participating in radical-radical chain termination reactions. Which of the two reactions of the adduct radical, the reaction with the saturated component or the reaction with the unsaturated component, dominates the kinetics of the process will depend on the reactivity and concentration ratios of the components in the binary system. In the

processes of this kind, in which an addend radical and a low-reactivity, inhibiting radical are involved in three types of quadratic-law chain termination reactions, the formation rate of the 1:1 adduct as a function of the concentration of the unsaturated component has a maximum (which usually occurs at a low concentration of this component).

Earlier [5,6], there were attempts to describe such peaking dependences fragmentarily, assuming that the saturated or unsaturated component is in excess, in terms of the direct and inverse proportionalities, respectively, that result from the simplification of a particular case of the kinetic equation set up by the quasi-steadystate treatment of binary copolymerization involving fairly long chains [5]. This specific equation is based on an irrational function, whose plot is a monotonic curve representing the dependence of the product formation rate on the concentration of the unsaturated component. This curve comes out of the origin of coordinates, is convex upward, and has an asymptote parallel to the abscissa axis. Replacing the component concentrations with the corresponding mole fractions generates a peak in this irrational function and thereby makes it suitable to describe the experimental data [7]. However, this circumstance cannot serve as a sufficient validation criterion for the mechanism examined, because the new property imparted to the function by the above artificial transformation does not follow from the solution of the set of algebraic equations that are set up for the reaction scheme accepted for the process in a closed system and express the equality of the steady-state formation and disappearance rates of the reactive intermediates.

This publication presents a comprehensive review of the nonbranched-chain kinetic models developed for particular types of additions of saturated free radicals to multiple bonds [8–14]. It covers free radical additions to olefins [10,11], their derivatives [8,9], formaldehyde (first compound in the aldehyde homological series) [8,9,12], and oxygen [13,14] (which can add an unsaturated radical as well) yielding various 1:1 molecular adducts, whose formation rates as a function of the unsaturated compound concentration pass through a maximum (free radical chain additions to the C=N bond have not been studied adequately). In the kinetic description of these nontelomerization chain processes, the reaction between the 1:1 adduct radical and the unsaturated molecule, which is in competition with chain propagation through a reactive free radical ($\cdot\text{PCl}_2$, $\text{C}_2\text{H}_5\dot{\text{C}}\text{HOH}$, etc.), is included for the first time in the chain propagation stage. This reaction yields a low-reactive radical (such as $\text{CH}_2=\text{C}(\text{CH}_3)\dot{\text{C}}\text{H}_2$ or $\text{H}\dot{\text{C}}=\text{O}$) and thus leads to chain termination because this radical does not continue the chain and thereby inhibits the chain process [8]. We will consider kinetic variants for the case of comparable component concentrations with an excess of the saturated component [10,11] and the

case of an overwhelming excess of the saturated component over the unsaturated component [8,9,12].

Based on the reaction schemes suggested for the kinetic description of the addition process, we have derived kinetic equations with one to three parameters to be determined directly. Reducing the number of unknown parameters in a kinetic equation will allow one to decrease the narrowness of the correlation of these parameters and to avoid a sharp buildup of the statistical error in the nonlinear estimation of these parameters in the case of a limited number of experimental data points [15]. The rate constant of the addition of a free radical to the double bond of the unsaturated molecule, estimated as a kinetic parameter, can be compared to its reference value if the latter is known. This provides a clear criterion to validate the mathematical description against experimental data. The kinetic equations were set up using the quasi-steady-state treatment. This method is the most suitable for processes that include eight to ten or more reactions and four to six different free radicals and are described by curves based on no more than three to seven experimental points. In order to reduce the exponent of the $2k_5[\text{R}_1]^2$ term in the $d[\text{R}_2]/dt = 0$ equation to unity [8], we used the following condition for the early stages of the process: $k_6 = \sqrt{2k_5 2k_7}$ [16] and, hence, $V_1 = V_5$

$+ 2V_6 + V_7 = (\sqrt{2k_5}[\text{R}_1\cdot] + \sqrt{2k_7}[\text{R}_2\cdot])^2$. Here, $[\text{R}_1\cdot]$ and $[\text{R}_2\cdot]$ are the concentrations of the addend radical and the low-reactive (inhibitor) radical, respectively; V_1 is the initiation rate; V_5 , $2V_6$, and V_7 are the rates of the three types of diffusion-controlled quadratic-law chain termination reactions; $2k_5$ and $2k_7$ are the rate constants of the loss of identical free radicals via the reactions $\text{R}_1\cdot + \text{R}_1\cdot$ and $\text{R}_2\cdot + \text{R}_2\cdot$, respectively; k_6 is the rate constant of the loss of different free radicals via the $\text{R}_1\cdot + \text{R}_2\cdot$ reaction (see Schemes 1–5). The kinetic equations thus obtained fit the peaking rate curves well throughout the range of unsaturated component concentrations in the binary systems. Our mathematical simulation was based on experimental data obtained for γ -radiation-induced addition reactions for which the initiation rate V_1 is known.

a) Addition to Olefins and Their Derivatives

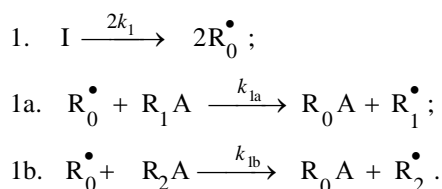
When reacting with olefins not inclined to free-radical polymerization, the free radicals originating from inefficient saturated telogens, such as alcohols [17] and amines [18], usually add to the least substituted carbon atom at the double bond, primarily yielding a free 1:1 adduct radical. This radical accumulates an energy of 90–130 kJ mol⁻¹, which is released upon the transformation of the C=C bond to an ordinary bond (according to the data reported for the addition of nonbranched C₁–C₄ alkyl radicals to propene and of similar C₁ and C₂ radicals to 1-butene in the gas phase under standard conditions [1–4]). Such adduct radicals, which do not decompose readily for structural reasons,

can abstract the most labile atom from a neighbor molecule of the saturated or unsaturated component of the binary reaction system, thus turning into a 1:1 adduct molecule. The consecutive and parallel reactions involved in this free-radical nonbranched-chain addition process are presented below (*Scheme 1*). In the case of comparable component concentrations with a nonoverwhelming excess of the saturated component, extra reaction (1b) ($k_{1b} \neq 0$) is included in the initiation stage [10,11]. In the case of an overwhelming excess of the saturated component reaction (1b) is ignored ($k_{1b} = 0$) [8,9,12].

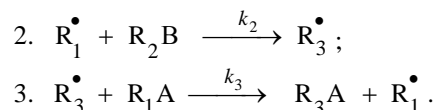
i. *Comparable Component Concentrations*

Scheme 1

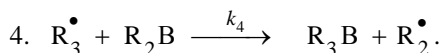
Chain initiation



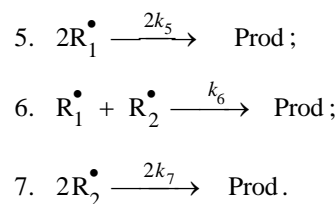
Chain propagation



Inhibition



Chain termination



In this scheme, I is an initiator (e.g., a peroxide [5,12,13]); R_0^\bullet is a reactive (initiating) radical; A and B are hydrogen or halogen atoms [2,5,17–24]; R_1^\bullet is $\cdot\text{PCl}_2$ [19], $\cdot\text{CCl}_3$ [20], alkyl [2,5], 1-hydroxyalkyl [5,6,17,22–24], or a similar functionalized reactive addend radical [5]; R_2^\bullet is an alkenyl radical (allyl or higher) [2,5,17–22], 1-hydroxyalkenyl [5,17,18,23,24], or a similar functionalized lowreactive (inhibitor) radical [5,18]; R_3^\bullet is a saturated reactive 1:1 adduct radical; R_0A , R_0B , and R_1A are saturated molecules; R_2B is an unsaturated molecule (olefin or its derivative); R_3A and R_3B are 1:1 adduct molecules; Prod designates the molecular products resulting from the dimerization or disproportionation of free radicals. The chain evolution (propagation and inhibition) stage of *Scheme 1* include consecutive reactions 2 and 3, parallel (competing) reaction pairs 3 and 4, and consecutiveparallel reaction pair 2-4.

The initiation reaction 1 is either the decomposition of a chemical initiator [5,17,18] or a reaction induced by light [5,17,18] or ionizing radiation [19–23]. The overall rate of chain initiation (reactions 1, 1a, and 1b) is determined by the rate of the ratelimiting step ($k_{1b} > k_{1a}$). The reaction between the free radical R_2^\bullet , which results from reactions 1b and 4, and the saturated molecule R_1A is energetically unfavorable because it implies the formation of the free radical R_1^\bullet , which is less stable than the initial one. The addition reaction 2 may be accompanied by the abstraction reaction 2a. $R_1^\bullet + R_2B \xrightarrow{k_{2a}} R_1B + R_2^\bullet$ which yields the product R_1B via a nonchain mechanism. Reaction 2a does not regenerate the addend radical R_1^\bullet and is not necessary for a kinetic description of the process, because the rate ratio of reactions 2 and 2a, $V_2/V_{2a} = k_2/k_{2a}$, is independent of the concentration of the unsaturated component R_2B in the system. The inhibition of the nonbranched-chain addition process is due to reaction 4, in which the adduct radical R_3^\bullet is spent in an inefficient way, since this reaction, unlike reaction 3, does not regenerate R_1^\bullet . The inhibiting effect is also due to the loss of chain carriers R_1^\bullet through their collisions with lowreactive unsaturated radicals R_2^\bullet , but to a much lesser extent.

The rates of the formation (V , $\text{mol dm}^{-3} \text{ s}^{-1}$) of the 1:1 adducts R_3A (via a chain mechanism) and R_3B (via a nonchain mechanism) in reactions 3 and 4 are given by the equations

$$V_3(R_3A) = \frac{[\gamma l / (\gamma l + x)] V_1 \alpha l k_2 x}{k_2 x^2 + (\alpha l + x) \sqrt{2k_5 V_1}}, \quad (1)$$

$$V_4(R_3B) = \frac{[\gamma l / (\gamma l + x)] V_1 k_2 x^2}{k_2 x^2 + (\alpha l + x) \sqrt{2k_5 V_1}}, \quad (2)$$

where V_1 is the rate of the initiation reaction 1; $l = [R_1A]$ and $x = [R_2B]$ are the molar concentrations of the initial components, with $l > x$; k_2 is the rate constant of the addition of the R_1^\bullet radical from the saturated component R_1A to the unsaturated molecule R_2B (reaction 2); and $\gamma = k_{1a}/k_{1b}$ and $\alpha = k_3/k_4$ are the rate constant ratios for competing (parallel) reactions (α is the first chain-transfer constant for the freeradical telomerization process [5]). The rate ratio for the competing reactions is $V_3/V_4 = \alpha l/x$, and the chain length is $\nu = V_3/V_1$.

Earlier mathematical simulation [8] demonstrated that replacing the adduct radical R_3 with the radical R_2 [5] in the reaction between identical radicals and in the reaction involving R_1 gives rise to a peak in the curve of the 1:1 adduct formation rate as a function of the concentration of the unsaturated component. Reaction 1b, which is in competition with reaction 1a, is responsible for the maximum in the curve described by Eq. (2), and reaction 4, which is in competition with

reaction (3), is responsible for the maximum in the curve defined by Eq. (1).

The number of unknown kinetic parameters to be determined directly (k_2 , α , and γ) can be reduced by introducing the condition $\gamma \cong \alpha$, which is suggested by the chemical analogy between the competing reactions pairs 1a–1b and 3–4. For example, the ratios of the rate constants of the reactions of $\cdot\text{OH}$, $\text{CH}_3\text{O}\cdot$, $\cdot\text{CH}_3$, $\text{NO}_3\cdot$, and $\text{H}_2\text{PO}_4\cdot$ with methanol to the rate constants of the reactions of the same radicals with ethanol in aqueous solution at room temperature are 0.4–0.5 [25,26]. For the same purpose, the rate constant of reaction 2 in the kinetic equation can be replaced with its analytical expression $k_2 = \alpha l_m \sqrt{2k_5 V_1 / x_m^2}$, which is obtained by solving the quadratic equation following from the reaction rate extremum condition $\partial V_{3,4} (1:1 \text{ Adduct}) / \partial x = 0$, where $V_{3,4} (1:1 \text{ Adduct}) = V_3 + V_4$. After these transformations, the overall formation rate equation for the 1:1 adducts R_3A and R_3B (which may be identical, as in the case of R_3H [5,8,9,12,13,18-21]), appears as

$$V_{3,4} (1:1 \text{ Adduct}) = \frac{V_1 \alpha k_2 x}{k_2 x^2 + (\alpha l + x) \sqrt{2k_5 V_1}} = (3)$$

$$V_{3,4} (1:1 \text{ Adduct}) = \frac{V_1 \alpha (1 - \chi) \chi}{\chi^2 + [\alpha(1 - \chi) + \chi] / \{ \alpha [(1/\chi_m) - 1]^2 - 1 \}}, \quad (3b)$$

where $1 - \chi = l/(l + x)$ and $\chi = x/(l + x)$ are the mole fractions of the components R_1A and R_2B ($0 < \chi < 1$), respectively, and χ_m is the χ value at the point of maximum.

The overall formation rate of the 1:1 adducts R_3A and R_3B is a sophisticated function of the formation and disappearance rates of the radicals $\text{R}_1\cdot$ and $\text{R}_2\cdot$:
 $V(\text{R}_3\text{A}, \text{R}_3\text{B}) = (V_{1a} + V_3 - V_5) - (V_{1b} + V_4 - V_7)$.

The application of the above rate equations to particular single nonbranched-chain additions is illustrated in Fig. 1. Curve 1 represents the results of simulation in terms of Eq. (3b) for the observed 1:1 adduct formation rate as a function of the mole fraction of the unsaturated component in the phosphorus trichloride–methylpropene¹ reaction system at 303 K [19]. In this simulation, the ⁶⁰Co γ -radiation dose rate was set at $P = 0.01 \text{ Gy s}^{-1}$ and the initiation yield was taken to be $G(\cdot\text{PCl}_2) = 2.8$ particles per 100 eV ($1.60 \times 10^{-17} \text{ J}$) of the energy absorbed by the solution [19]. The product of reaction 3 is $\text{Cl}_2\text{PCH}_2\text{C}(\text{Cl})(\text{CH}_3)\text{CH}_3$ (two isomers), $V_1 = 4.65 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$ at $\chi = 0$, and $2k_5 = 3.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This leads to $\alpha = (2.5 \pm 0.4) \times 10^3$, and the rate constant of reaction 2 derived from this α value is $k_2 = (1.1 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

¹In an earlier work [10], the methylpropene concentration in this system was overvalued by a factor of 1.7 when it was derived from the mole fractions given in [19].

$$= \frac{V_1 \alpha l x}{x^2 + (\alpha l + x) x_m^2 / \alpha l_m}, \quad (3a)$$

where l_m and x_m are the component concentrations l and x at the points of maximum of the function. Provided that V_1 is known, the only parameter in Eq. (3a) to be determined directly is α . If V_1 is known only for the saturated component R_1A , then, for the binary system containing comparable R_1A and R_2B concentrations, it is better to use the quantity λV_1 , where $\lambda = l/(l + x)$ is the mole fraction of R_1A , in place of V_1 in Eqs. (3) and (3a).

The two variable concentrations in the kinetic equation (3) – l and x – can be reduced to one variable by replacing them with the corresponding mole fractions. Substituting the expression $k_2 = \{ \alpha [(1/\chi_m) - 1]^2 - 1 \} 2k_5 V_1 / (l_m + x_m)$, derived from the rate extremum condition, into this transformed equation for the binary system containing comparable component concentrations, we obtain

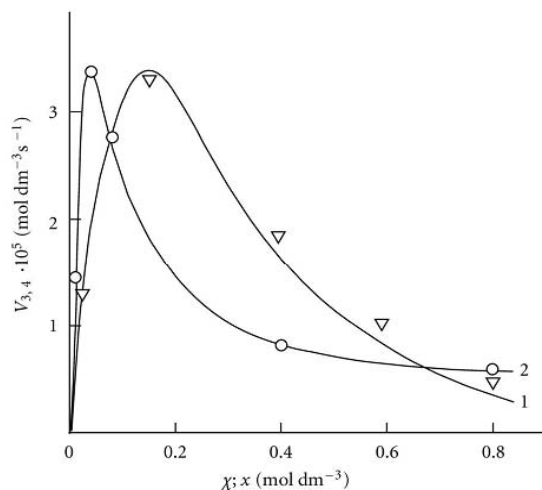


Fig. 1 : Reconstruction of the functional dependences (curves) of the product formation rates $V_{3,4}$ (∇) on the mole fraction of the unsaturated component (χ) from empirical data (symbols) using Eq. (3b) (model optimization with respect to the parameter α) for the phosphorus trichloride–methylpropene reaction system at 303 K [19] (standard deviation of $S_\gamma = 2.58 \times 10^{-6}$) and (\circ) on the concentration of the unsaturated component (x) from empirical data (symbols) using Eq. (4a) (model optimization with respect to V_1 , x_m , and α) for the 2-propanol–2-propen-1-ol system at 433 K [23] ($S_\gamma = 5.91 \times 10^{-7}$).

Note that, if the R_2-B bond dissociation energy for the unsaturated component of the binary system is approximately equal to or above, not below, the R_1-A bond dissociation energy for the saturated component, than the rate of reaction 4 relative to the rate of the parallel reaction 3 (chain propagation through the reactive free radical $R_1\cdot$) will be sufficiently high for adequate description of R_3A and R_3B adduct formation in terms of Eqs. (1)–(3b) only at high temperatures [20]. In the phosphorus trichloride–propene system, the difference between the R_2-B ($B = H$) and R_1-A ($A = Hal$) bond dissociation energies in the gas phase under standard conditions [1] is as small as 5 kJ mol^{-1} , while in the tetrachloromethane–methylpropene (or cyclohexene) and bromoethane–2-methyl–2-butene systems, this difference is 20.9 (37.7) and $\sim 24 \text{ kJ mol}^{-1}$, respectively.

ii. *Excess of the Saturated Component*

If the concentration of the saturated component exceeds the concentration of the unsaturated component in the binary system, reaction 1b can be neglected. If this is the case ($k_{1b} = 0$), then, in the numerators of the rate equations for reactions 3 and 4 (Eqs. (1) and (2)), $\gamma l / (\gamma l + x) = 1$ and the overall rate equation for the formation of the 1:1 adducts R_3A and R_3B will appear as =

$$V_{3,4} (1:1 \text{ Adduct}) = \frac{V_1(al + x)k_2x}{k_2x^2 + (al + x)\sqrt{2k_5V_1}} = \quad (4)$$

$$= \frac{V_1x}{\frac{x^2}{al + x} + \left(\frac{\sqrt{al}m}{x_m} + \frac{1}{\sqrt{al}m} \right)^{-2}} \quad (4a)$$

where the parameters are designated in the same way as in Eqs. (1)–(3a), $l \gg x$, and $k_2 = [(\sqrt{al}m / x_m) + (1/\sqrt{al}m)]^2 \sqrt{2k_5V_1}$ is determined from the condition $\partial V_{3,4} (1:1\text{Adduct}) / \partial x = 0$.

The rate equations for the chain termination reactions 5–7 (*Scheme 1*, $k_{1b} = 0$) are identical to Eqs. (9)–(11) (see below) with $\beta = 0$.

Note that, if it is necessary to supplement *Scheme 1* for $k_{1b} = 0$ with the formation of R_1B via the possible nonchain reaction 2a (which is considered in the Section a), the parameter k_{2a} should be included in the denominator of Eq. (4) to obtain $k_2x^2 + (al+x) (k_{2a}x + \sqrt{2k_5V_1})$.

The analytical expression for k_2 in the case of $k_{2a} \neq 0$ is identical to the expression for k_2 for Eq. (4). The equation for the rate $V_{2a}(R_1B)$ can be derived by replacing k_2 with k_{2a} in the numerator of Eq. (4) containing k_{2a} in its denominator.

Curve 2 in Fig. 1 illustrates the good fit between Eq. (4a) and the observed 1:1 adduct formation rate as

a function of the concentration of the unsaturated component in the reaction system 2-propanol–2-propen-1-ol at 433 K [8,9]. In this description, we used a ^{60}Co γ -radiation dose rate of $P = 4.47 \text{ Gy s}^{-1}$ [23]. The product of reactions 3 and 4 is $\text{CH}_3(\text{CH}_3)\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, and $2k_5 = 1.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The following parameters were obtained: $V_1 = (3.18 \pm 0.4) \times 10^6 \text{ mol dm}^{-3} \text{ s}^{-1}$, $x_m = (3.9 \pm 0.5) \times 10^{-2} \text{ mol dm}^{-3}$, and $\alpha = (6.8 \pm 0.8) \times 10^{-2}$. The rate constant of reaction 2 derived from this α is $k_2 = (1.0 \pm 0.14) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

b) *Addition to Formaldehyde*

Free radicals add to the carbon atom at the double bond of the carbonyl group of dissolved free (unsolvated, monomer) formaldehyde. The concentration of free formaldehyde in the solution at room temperature is a fraction of a percent of the total formaldehyde concentration, which includes formaldehyde chemically bound to the solvent [27]. The concentration of free formaldehyde exponentially increases with increasing temperature [28]. The energy released as a result of this addition, when the $\text{C}=\text{O}$ bond is converted into an ordinary bond, is 30 to 60 kJ mol^{-1} (according to the data on the addition of $\text{C}_1\text{--C}_4$ alkyl radicals in the gas phase under standard conditions [1–4]). The resulting free 1:1 adduct radicals can both abstract hydrogen atoms from the nearest-neighbor molecules of the solvent or unsolvated formaldehyde and, due to its structure, decompose by a monomolecular mechanism including isomerization [9,12].

i. *Addition of Free 1-Hydroxyalkyl Radicals with Two or More Carbon Atoms*

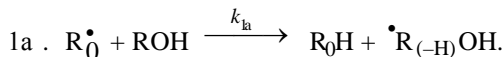
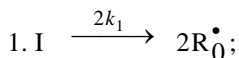
Free 1-hydroxyalkyl radicals (which result from the abstraction of a hydrogen atom from the carbon atom bonded to the hydroxyl group in molecules of saturated aliphatic alcohols but methanol under the action of chemical initiators [29,30], light [17,31], or ionizing radiation [32,33]) add at the double bond of free formaldehyde dissolved in the alcohol, forming 1,2-alkanediols [8,9,12,29–36], carbonyl compounds, and methanol [8,33] via the chaining mechanism. (The yields of the latter two products in the temperature range of 303 to 448 K are one order of magnitude lower.) In these processes, the determining role in the reactivity of the alcohols can be played by the desolvation of formaldehyde in alcohol–formaldehyde solutions, which depends both on the temperature and on the polarity of the solvent [28,33]. For the γ -radiolysis of 1(or 2)-propanol–formaldehyde system at a constant temperature, the dependences of the radiation-chemical yields of 1,2-alkanediols and carbonyl compounds as a function of the formaldehyde concentration show maxima and are symbatic [8,32]. For a constant total formaldehyde concentration of 1 mol dm^{-3} , the dependence of the 1,2-alkanediol yields as a function of

temperature for 303–473 K shows a maximum, whereas the yields of carbonyl compounds and methanol increase monotonically [33] (along with the concentration of free formaldehyde [28]). In addition to the above products, the nonchain mechanism in the γ -radiolysis of the solutions of formaldehyde in ethanol

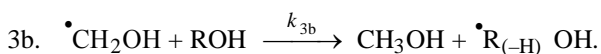
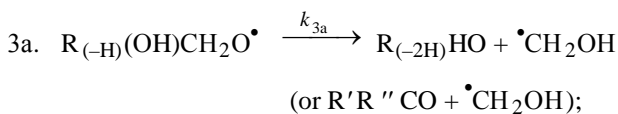
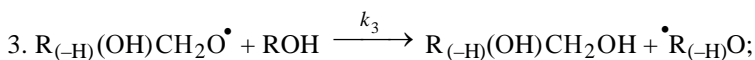
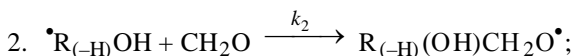
and 1- and 2-propanol gives ethanediol, carbon monoxide, and hydrogen in low radiation-chemical yields (which, however, exceed the yields of the same products in the γ -radiolysis of individual alcohols) [8,9,33]. The available experimental data can be described in terms of the following scheme of reactions:

Scheme 2

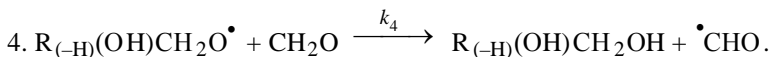
Chain initiation



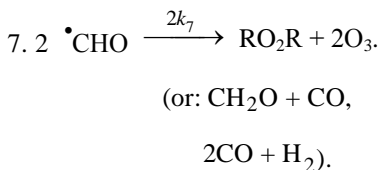
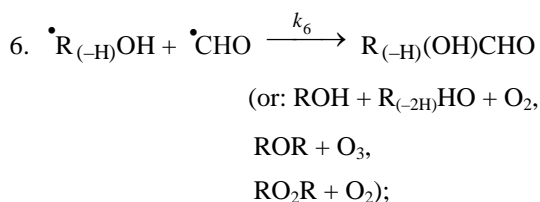
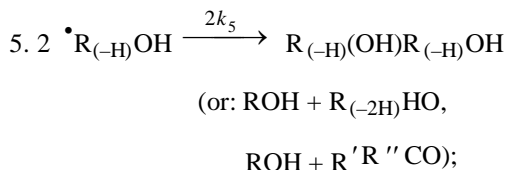
Chain propagation



Inhibition



Chain termination



In these reactions, I is an initiator, e.g., a peroxide [29,30]; R_0^\bullet , some reactive radical (initiator radical); R, an alkyl; ROH, a saturated aliphatic alcohol, either primary or secondary, beginning from ethanol; CH_2O , the unsaturated molecule – free formaldehyde;

$\bullet CH_2OH$, the 1-hydroxymethyl fragment radical; $\bullet R_{(-H)}OH$, the reactive 1-hydroxyalkyl radical (adduct radical), beginning from 1-hydroxyethyl; $\bullet CHO$, the low-reactive formyl radical (inhibitor); R_0H , the molecular product; $R_{(-H)}(OH)CH_2OH$, 1,2-alkanediol; $R_{(-2H)}HO$, an aldehyde

$\beta = k_{3a}/k_4$ (mol dm⁻³) are the ratios of the rate constants of the competing (parallel) reactions. Estimates of $2k_5$ were reported by Silaev *et al.* [39,40]. From the extremum condition for the reaction 3a rate function, $\partial V_{3a} / \partial x = 0$, we derived the following analytical expression: $k_2 = (aI_m + \beta) \sqrt{2k_5 V_1 / x^2 m}$.

The overall process rate is a complicated function of the formation and disappearance rates of the $\cdot R_{(-H)}OH$ and $\cdot CHO$ free radicals: $V(R_{(-H)}(OH)CH_2OH, R_{(-2H)}HO, CH_3OH) = V_{1a} + V_3 + V_{3b} - V_4 - V_5 + V_7$. The ratios of the rates of the competing reactions are $V_3/V_4 = aI/x$ and $V_{3a}/V_4 = \beta/x$, and the chain length is $\nu = (V_3 + V_{3a})/V_1$. The ratio of the rates of formation of 1,2-alkanediol and the carbonyl compound is a simple linear function of x : $V_{3,4}(R_{(-H)}(OH)CH_2OH)/V_{3a}(R_{(-2H)}HO) = (k_4/k_{3a})x + (k_3/k_{3a})I$. The equations for the rates of chain-termination reactions 5–7 are identical to Eqs. (9)–(11) (see below).

Figure 2 illustrates the use of Eqs. (5) and (6) for describing the experimental dependences of the formation rates of 1,2-butanediol (curve 1) in reactions 3 and 4 and propanal (curve 2) in reaction 3a on the concentration of free formaldehyde in the 1-propanol–formaldehyde reacting system at a total formaldehyde concentration of 2.0 to 9.5 mol dm⁻³ and temperature of 413 K [8,9,41]. The concentration dependence of the propanal formation rate was described using the estimates of kinetic parameters obtained for the same dependence of the 1,2-butanediol formation rate. We considered these data more reliable for the reason that the carbonyl compounds forming in the alcohol–formaldehyde systems can react with the alcohol and this reaction depends considerably on the temperature and acidity of the medium [27]. The mathematical modeling of the process was carried out using a ¹³⁷Cs γ -radiation dose rate of $P = 0.8$ Gy s⁻¹ [32,41], a total initiation yield of $G(CH_3CH_2\dot{C}HOH) = 9.0$ particles per 100 eV [8,9] ($V_1 = 4.07 \times 10^{-7}$ mol dm⁻³ s⁻¹), and $2k_5 = 4.7 \times 10^9$ dm³ mol⁻¹ s⁻¹). The following values of the parameters were obtained: $\alpha = 0.36 \pm 0.07$, $\beta = 0.25 \pm 0.05$ mol dm⁻³, and $k_2 = (6.0 \pm 1.4) \times 10^3$ dm³ mol⁻¹ s⁻¹.

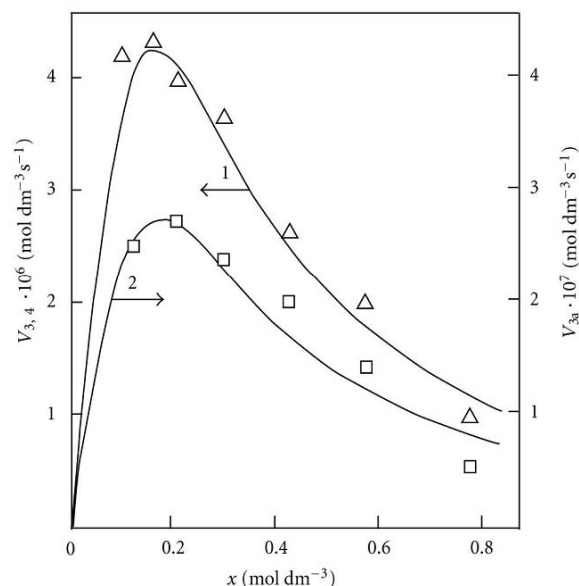


Fig. 2 : Reconstruction of the functional dependence (curves) of the product formation rates $V_{3,4}$ and V_{3a} on the concentration x of free formaldehyde (model optimization with respect to the parameters α , β and k_2) from empirical data (symbols) for the 1-propanol–formaldehyde system at 413 K [8,9,41]: (1, Δ) calculation using Eq. (5), standard deviation of $S_\gamma = 2.20 \times 10^{-7}$; (2, \square) calculation using Eq. (6), $S_\gamma = 2.38 \times 10^{-8}$.

Note that, as compared to the yields of 1,2-propanediol in the γ -radiolysis of the ethanol–formaldehyde system, the yields of 2,3-butanediol in the γ -radiolysis of the ethanol–acetaldehyde system are one order of magnitude lower [41]. Using data from [8,9], it can be demonstrated that, at 433 K, the double bond of 2-propen-1-ol accepts the 1-hydroxyethyl radical 3.4 times more efficiently than the double bond of formaldehyde [42].

ii. Addition of the Hydroxymethyl Radical

The addition of hydroxymethyl radicals to the carbon atom at the double bond of free formaldehyde molecules in methanol, initiated by the free-radical mechanism, results in the chain formation of ethanediol [34]. In this case, reaction 3a in Scheme 2 is the reverse of reaction 2, the 1-hydroxyalkyl radical $\cdot R_{(-H)}OH$ is the hydroxymethyl radical $\cdot CH_2OH$, so reaction 3b is eliminated ($k_{3b} = 0$), and reaction 5 yields an additional amount of ethanediol via the dimerization of chain-carrier hydroxymethyl radicals (their disproportionation can practically be ignored [43]). The scheme of these reactions is presented in [35].

The rate equation for ethanediol formation by the chain mechanism in reaction 3 and by the nonchain mechanism in reactions 4 and 5 in the methanol–formaldehyde system has a complicated form³ as compared to Eq. (1) for the formation rate of the other 1,2-alkanediols [12]:

³The alcohol concentration in alcohol–formaldehyde solutions at any temperature can be estimated by the method suggested in [38,39]. The data necessary for estimating the concentration of free formaldehyde using the total formaldehyde concentration in the solution are reported by Silaev *et al.* [28,39].

$$V_{3,4,5}(\text{CH}_2\text{OH})_2 = V_1 [f(\alpha l + x)k_2x + V_1 2k_5(\alpha l + \beta + x)^2] / f^2 \quad (7)$$

where $f = k_2x^2 + (\alpha l + \beta + x) \sqrt{2k_5V_1}$.

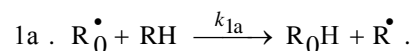
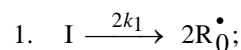
If the rate of ethanediol formation by the dimerization mechanism in reaction 5 is ignored for the reason that it is small as compared to the total rate of ethanediol formation in reactions 3 and 4, Eq. (7) will be identical to Eq. (5). After the numerator and denominator on the right-hand side of Eq. (5) are divided by $k_{-2} \equiv k_{3a}$, one can replace k_2 in this equation with $K_2 = k_2/k_{-2}$, which is the equilibrium constant for the reverse of reaction 2. Ignoring the reverse of reaction 2 ($k_{3a} = 0$, $\beta = 0$) makes Eq. (5) identical to Eq. (4) in Scheme 1 (see the Section a). In this case, the rate constant k_2 is effective.

c) Addition to Oxygen

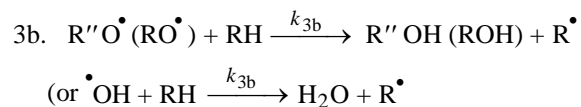
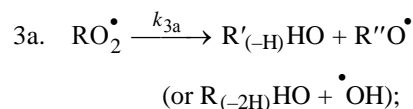
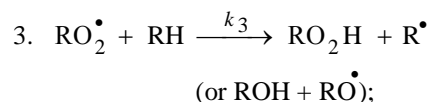
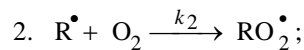
The addition of a free radical or an atom to one of the two multiply bonded atoms of the oxygen molecule yields a peroxy free radical and thus initiates oxidation, which is the basic process of chemical evolution. The peroxy free radical then abstracts the most labile atom from a molecule of the compound being oxidized or decomposes to turn into a molecule of an oxidation product. The only reaction that can compete with these two reactions at the chain evolution stage is the addition of the peroxy radical to the oxygen molecule (provided that the oxygen concentration is sufficiently high). This reaction yields a secondary,

Scheme 3

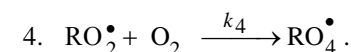
Chain initiation



Chain propagation



Inhibition



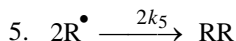
tetraoxyalkyl, 1:2 adduct radical, which is the heaviest and the largest among the reactants. It is less reactive than the primary, 1:1 peroxy adduct radical and, as a consequence, does not participate in further chain propagation. At moderate temperatures, the reaction proceeds via a nonbranched chain mechanism.

i. Addition of Hydrocarbon Free Radicals

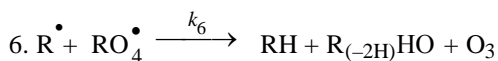
Usually, the convex curve of the hydrocarbon (RH) autooxidation rate as a function of the partial pressure of oxygen ascends up to some limit and then flattens out [6]. When this is the case, the oxidation kinetics is satisfactorily describable in terms of the conventional reaction scheme [2,5,6,16,44,45], which involves two types of free radicals. These are the hydrocarbon radical R^\bullet (addend radical) and the addition product RO_2^\bullet (1:1 adduct radical). However, the existing mechanisms are inapplicable to the cases in which the rate of initiated oxidation as a function of the oxygen concentration has a maximum (Figs. 3, 4) [46,47]. Such dependences can be described in terms of the competition kinetics of free-radical chain addition, whose reaction scheme involves not only the above two types of free radicals, but also the RO_4^\bullet radical (1:2 adduct) inhibiting the chain process [13,14].

³In an earlier publication [8], this equation does not take into account reaction 3a.

Chain termination



(or $R_{(-2H)}H + RH$);

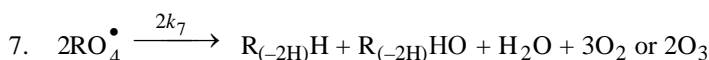


(or: $R_{(-2H)}H + R_{(-2H)}HO + H_2O + O_2$,

$ROH + R_{(-2H)}HO + O_2$,

$ROR + O_3$,

$RO_2R + O_2$);



(or: $ROH + R_{(-2H)}HO + 3O_2 \text{ or } 2O_3$,

$2R_{(-2H)}HO + H_2O_2 + 2O_2$,

$2R_{(-2H)}HO + H_2O + O_3 + O_2$,

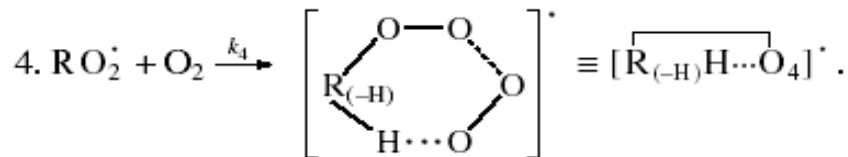
$RO_2R + 3O_2 \text{ or } 2O_3$).

The only difference between the kinetic model of oxidation represented by *Scheme 3* and the kinetic model of the chain addition of 1-hydroxyalkyl radicals to the free (unsolvated) form of formaldehyde in nonmethanolic alcohol-formaldehyde systems [8,9] (*Scheme 2*, Section b) is that in the former does not include the formation of the molecular 1:1 adduct *via* reaction 4.

The decomposition of the initiator I in reaction 1 yields a reactive R_0^{\bullet} radical, which turns into the ultimate product R_0H *via* reaction 1a, generating an alkyl radical R^{\bullet} , which participates in chain propagation. In reaction 2, the addition of the free radical R^{\bullet} to the oxygen molecule yields a reactive alkylperoxyl 1:1 adduct radical RO_2^{\bullet} [45], which possesses increased energy owing to the energy released upon the conversion of the O=O bond into the ordinary bond RO-O \cdot (for addition in the gas phase under standard conditions, this energy is 115–130 kJ mol⁻¹ for C₁–C₄ alkyl radicals [1,2,4] and 73 kJ mol⁻¹ for the allyl radical [4]). Because of this, the adduct radical can decompose (reaction 3a) or react with some neighbor molecule (reaction 3 or 4) on the spot, without diffusing in the solution and, accordingly, without entering into any chain termination reaction. In reaction 3, the interaction between the radical adduct RO_2^{\bullet} and the hydrocarbon molecule RH yields, *via* a chain mechanism, the alkyl hydroperoxide RO_2H (this reaction regenerates the chain carrier R^{\bullet} and, under certain conditions, can be viewed as being reversible [2]) or the alcohol ROH (this is followed by the regeneration of R^{\bullet} *via* reaction 3b). The latter

(alternative) pathway of reaction 3 consists of four steps, namely, the breaking of old bonds and the formation of two new bonds in the reacting structures. In reaction 3a, the isomerization and decomposition of the alkylperoxyl radical adduct RO_2^{\bullet} with O–O and C–O or C–H bond breaking take place [6,44], yielding the carbonyl compound $R'_{(-H)}HO$ or $R_{(-2H)}HO$. Reaction 3b produces the alcohol $R''OH$ or water and regenerates the free radical R^{\bullet} (here, R' and R'' are radicals having a smaller number of carbon atoms than R). As follows from the above scheme of the process, consecutive reactions 3a and 3b (whose rates are equal within the quasi-steady-state treatment), in which the highly reactive fragment, oxyl radical $R''O^{\bullet}$ (or $\cdot OH$) forms and then disappears, respectively, can be represented as a single, combined bimolecular reaction 3a, b occurring in a "cage" of solvent molecules. Likewise, the alternative (parenthesized) pathways of reactions 3 and 3b, which involve the alkoxy radical RO^{\bullet} , can formally be treated as having equal rates. For simple alkyl C₁–C₄ radicals R, the pathway of reaction 3 leading to the alkyl hydroperoxide RO_2H is endothermic ($\Delta H^{\circ}_{298} = 30\text{--}80$ kJ mol⁻¹) and the alternative pathway yielding the alcohol ROH is exothermic ($\Delta H^{\circ}_{298} = -120$ to -190 kJ mol⁻¹), while the parallel reaction 3a, which yields a carbonyl compound and the alkoxy radical $R''O^{\bullet}$ or the hydroxyl radical $\cdot OH$, is exothermic in both cases ($\Delta H^{\circ}_{298} = -80$ to -130 kJ mol⁻¹), as also is reaction 3b ($\Delta H^{\circ}_{298} = -10$ to -120 kJ mol⁻¹), consecutive to reaction 3a, according to thermochemical data for the gas phase [2–4]. In reaction 4, which is competing with (parallel to)

reactions 3 and 3a (chain propagation through the reactive radical R[•]), the resulting low-reactive radical that does not participate in further chain propagation and inhibits the chain process is supposed to be the alkyltetraoxyl 1:2 radical adduct^{4,5} RO₄[•], which has the largest weight and size. This radical is possibly



Reaction 4 in the case of the methylperoxyl radical CH₃O₂[•] adding to the oxygen molecule to yield the methyltetraoxyl radical CH₃O₄[•] takes place in the gas phase, with heat absorption equal to 110.0 ± 18.6 kJ mol⁻¹ [20] (without the energy of the possible formation of a hydrogen bond taken into account). The exothermic reactions 6 and 7, in which the radical R[•] or RO₄[•] undergoes disproportionation, include the isomerization and decomposition of the RO₄[•] radical (taking into account the principle of detailed balance for the various reaction pathways). The latter process is likely accompanied by chemiluminescence typical of hydrocarbon oxidation [23]. These reactions regenerate oxygen as O₂ molecules (including singlet oxygen⁵ [23, 30]) and, partially, as O₃ molecules and yield the carbonyl compound R_(-2H)HO (possibly in the triplet excited state [23]). Depending on the decomposition pathway, the other possible products are the alcohol ROH, the ether ROR, and the alkyl peroxide RO₂R. It is likely that the isomerization and decomposition of the RO₄[•] radical *via* reactions 6 and 7 can take place through the breaking of a C–C bond to yield carbonyl compounds, alcohols,

⁴It is hypothesized that raising the oxygen concentration in the *o*-xylene–oxygen system can lead to the formation of an [RO[•] ⋯ O₂] intermediate complex [46] similar to the [ROO[•] ⋯ (π-bond)RH] complex between the alkylperoxyl 1:1 adduct radical and an unsaturated hydrocarbon suggested in this work. The electronic structure of the π-complexes is considered elsewhere [48].

⁵Thermochemical data are available for some polyoxyl free radicals (the enthalpy of formation of the methyltetraoxyl radical without the energy of the possible intramolecular hydrogen bond H⋯O taken into account is ΔH_{f, 298}(CH₃O₄[•]) = 121.3 ± 15.3 kJ mol⁻¹) and polyoxides (ΔH_{f, 298}(CH₃O₄H) = -21.0 ± 9 kJ mol⁻¹) [49]. These data were obtained using the group contribution approach. Some physicochemical and geometric parameters were calculated for the methyl hydrotetraoxide molecule as a model compound [50–52]. The IR spectra of dimethyl tetraoxide with isotopically labeled groups in Ar–O₂ matrices were also reported [53]. For reliable determination of the number of oxygen atoms in an oxygen-containing species, it is necessary to use IR and EPR spectroscopy in combination with the isotope tracer method [53].

⁶The $\overline{\text{R}_{(-\text{H})}\text{H} \cdots \text{O}(\text{R})\text{O}_3}$ ring consisting of the same six atoms (C, H, and 4O), presumably with a hydrogen bond [6], also forms in the transition state of the dimerization of primary and secondary alkylperoxyl radicals RO₂[•] *via* the Russell mechanism [5,55].

stabilized by a weak intramolecular H⋯O hydrogen bond [54] shaping it into a six-membered cyclic structure⁶ (seven-membered cyclic structure in the case of aromatic and certain branched acyclic hydrocarbons) [56,57]:

ethers, and organic peroxides containing fewer carbon atoms than the initial hydrocarbon, as in the case of the alkylperoxyl radical RO₂[•] in reaction 3a. At later stages of oxidation and at sufficiently high temperatures, the resulting aldehydes can be further oxidized into respective carboxylic acids. They can also react with molecular oxygen so that a C–H bond in the aldehyde molecule breaks to yield two free radicals (HO₂[•] and [•]R_{(-H)O} or [•]R_{(-2H)O}). This process, like possible ozone decomposition yielding an [•]O atom or peroxide decomposition with O–O bond breaking, leads to degenerate chain branching [5].

The equations describing the formation rates of molecular products at the chain propagation and termination stages of the above reaction scheme, set up using the quasi-steady-state treatment, appear as follows:

$$V_3(\text{RO}_2\text{H}; \text{ROH}) = V_1 \alpha k_2 x / f = \quad (8)$$

$$= V_1 \alpha x / f_m, \quad (8a)$$

$$V_{3a}(\text{R}'_{(-\text{H})}\text{HO}; \text{R}_{(-2\text{H})}\text{HO}) = V_{3b}(\text{R}''\text{OH}; \text{H}_2\text{O}) =$$

$$= V_1 \beta k_2 x / f = \quad (9)$$

$$= V_1 \beta x / f_m, \quad (9a)$$

$$V_5 = V_1^2 2k_5 (\alpha l + \beta + x)^2 / f^2, \quad (10)$$

$$2V_6 = 2V_1 \sqrt{2k_5 V_1 (\alpha l + \beta + x) k_2 x^2 / f^2}, \quad (11)$$

$$V_7 = V_1 (k_2 x^2)^2 / f^2, \quad (12)$$

where V₁ is the initiation rate, l = [RH] and x = [O₂] are the molar concentrations of the starting components (l ≫ x), α = k₃/k₄ and β = k_{3a}/k₄ (mol dm⁻³) are the ratios of the rate constants of the competing (parallel)

⁷Note that the alkylperoxyl radicals RO₂[•] are effective quenchers of singlet oxygen O₂(¹Δ_g) [58].

reactions, $k_2 = (al_m + \beta) \sqrt{2k_5V_1} / x_m^2$ is the rate constant of the addition of the alkyl radical R^\bullet to the oxygen molecule (reaction 2) as determined by solving the quadratic equation following from the rate function extremum condition $\partial V_{3,3a} / \partial x = 0$, l_m and x_m are the values of l and x at the maximum point of the function, and $f = k_2x^2 + (al + \beta + x) \sqrt{2k_5V_1}$, and $f_m = x^2 + (al + \beta + x) x_m^2 (al_m + \beta)$.

The ratios of the rates of the competing reactions are $V_3/V_4 = al/x$ and $V_{3a}/V_4 = \beta/x$, and the chain length is $\nu = (V_3 + V_{3a})/V_1$. Eq. (9) is identical to Eq. (6). Eqs (8a) and (9a) were obtained by replacing the rate constant k_2 in Eqs. (8) and (9) with its analytical expression (for reducing the number of unknown parameters to be determined directly).

For $al \gg \beta$ ($V_3 \gg V_{3a}$), when the total yield of alkyl hydroperoxides and alcohols having the same number of carbon atoms as the initial compound far exceeds the yield of carbonyl compounds, as in the case of the oxidation of some hydrocarbons, the parameter β in Eqs. (8) and (8a) can be neglected ($\beta = 0$) and these equations become identical to Eqs. (3) and (3a) with the corresponding analytical expression for k_2 .

In the alternative kinetic model of oxidation, whose chain termination stage involves, in place of R^\bullet (Scheme 3), RO_2^\bullet radicals reacting with one another and with RO_4^\bullet radicals, the dependences of the chain formation rates of the products on the oxygen concentration x derived by the same method have no maximum: $V_3 = V_1 k_3 l / (k_4 x + \sqrt{2k_5 V_1})$ and $V_{3a} = V_1 k_{3a} (k_4 x + \sqrt{2k_5 V_1})$. In the kinetic model of oxidation that does not include the competing reaction 4 ($k_4 = 0$) and involves the radicals R^\bullet and RO_2^\bullet (the latter instead of RO_4^\bullet in Scheme 3) in reactions 5–7, the reaction rate functions V_3 and V_{3a} obtained in the same way are fractional rational functions in the form of $a_0 x / (b_0 x + c_0)$, where a_0 , b_0 , and c_0 are coefficients having no extremum. For a similar kinetic model in which reactions 3a,b and 4 appearing in the above scheme are missing ($k_{3a} = k_4 = 0$), Walling [5], using the quasi-steady-state treatment in the long kinetic chain approximation, when it can be assumed that $V_2 = V_3$, without using the substitution $k_6 = \sqrt{2k_5 2k_7}$ [5,6,16] (as distinct from this work), found that $V_2 = V_3$ is an irrational function of x : $a_1 x / \sqrt{b_1 x^2 + c_1 x + d_1}$ where a_1 , b_1 , c_1 , and d_1 are coefficients. Again, this function has no maximum with respect to the concentration of any of the two components.

Thus, of the three kinetic models of oxidation mathematically analyzed above, which involve the radicals R^\bullet and RO_2^\bullet in three types of quadratic-law chain termination reactions (reactions 5–7) and are variants of the conventional model [2,5,6,16,44,45], the

last two lead to an oxidation rate versus oxygen concentration curve that emanates from the origin of coordinates, is convex upward, and has an asymptote parallel to the abscissa axis. Such monotonic dependences are observed when the oxygen solubility in the liquid is limited under given experimental conditions and the oxygen concentration attained⁸ is $[O_2]_{top} \leq x_m$.

Unlike the conventional model, the above kinetic model of free-radical nonbranched chain oxidation, which includes the pairs of competing reactions 3–4 and 3a–4 (Scheme 3), allows us to describe the nonmonotonic (peaking) dependence of the oxidation rate on the oxygen concentration (Fig. 3). In this oxidation model, as the oxygen concentration in the binary system is increased, oxygen begins to act as an oxidation autoinhibitor or an antioxidant via the further oxidation of the alkylperoxyl 1:1 adduct radical RO_2^\bullet into the low-reactive 1:2 adduct radical RO_4^\bullet (reactions 4 and 6 lead to inefficient consumption of the free radicals RO_2^\bullet and R^\bullet and cause shortening of the kinetic chains). The optimum oxygen concentration x_m , at which the oxidation rate is the highest, can be calculated using kinetic equations (8a) and (9a) and Eq. (3a) with $\beta = 0$ or the corresponding analytical expression for k_2 . In the familiar monograph *Chain Reactions* by Semenov [60], it is noted that raising the oxygen concentration when it is already sufficient usually slows down the oxidation process by shortening the chains. The existence of the upper (second) ignition limit in oxidation is due to chain termination in the bulk through triple collisions between an active species of the chain reaction and two oxygen molecules (at sufficiently high oxygen partial pressures). In the gas phase at atmospheric pressure, the number of triple collisions is roughly estimated to be 10^3 times smaller than the number of binary collisions (and the probability of a reaction taking place depends on the specificity of the action of the third particle).

Curve 1 in Fig. 3 illustrates the fit between Eq. (3a) at $al \gg \beta$ and experimental data for the radiation-induced oxidation of *o*-xylene in the liquid phase at 373 K in the case of 2-methylbenzyl hydroperoxide forming much more rapidly than *o*-tolualdehyde ($V_3 \gg V_{3a}$ and $al \gg \beta$) [46]. The oxygen concentration limit in *o*-xylene is reached at an oxygen concentration of $[O_2]_{top} > x_m$, which corresponds to the third experimental point [46]. The oxygen concentration was calculated from the oxygen solubility in liquid xylene at 373 K [61]. The following quantities were used in this mathematical

⁸The oxygen concentration attained in the liquid may be below the thermodynamically equilibrium oxygen concentration because of diffusion limitations hampering the establishment of the gas–liquid saturated solution equilibrium under given experimental conditions (for example, when the gas is bubbled through the liquid) or because the Henry law is violated for the given gas–liquid system under real conditions.

description: ^{60}Co γ -radiation dose rate of $P = 2.18 \text{ Gy s}^{-1}$ and total initiation yield of $\text{G}(\text{o-CH}_3\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2) = 2.6$ particles per 100 eV of the energy absorbed by the solution [46]; $V_1 = 4.73 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$, and $2k_5 = 1.15 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The resulting value of the parameter α is $(9.0 \pm 1.8) \times 10^{-3}$; hence, $k_2 = (3.2 \pm 0.8) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. From the data presented in [62], it was estimated that $k_4 = k_3/\alpha = (5.2 \pm 1.2) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

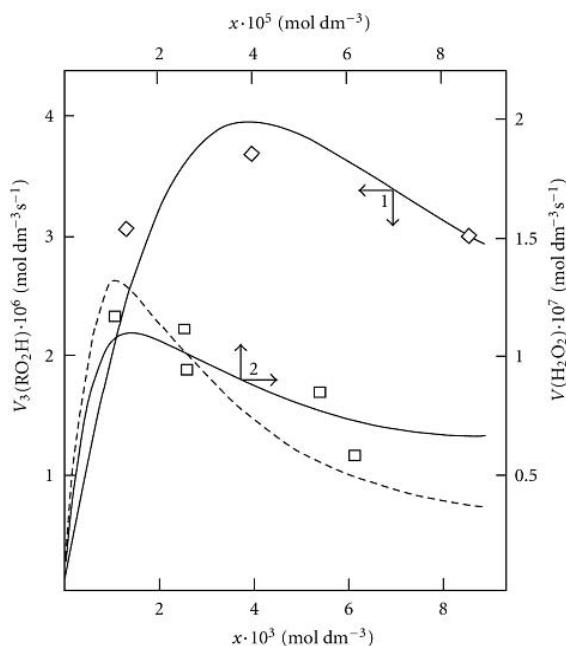


Fig. 3 : (1, \diamond) Reconstruction of the functional dependence of the 2-methylbenzyl hydroperoxide formation rate $V_3(\text{RO}_2\text{H})$ on the dissolved oxygen concentration x from empirical data (points) using Eq. (3a) (model optimization with respect to the parameter α) for the *o*-xylene–oxygen system at 373 K [46] (standard deviation of $S_\gamma = 5.37 \times 10^{-7}$). (2, \square) Reconstruction of the functional dependence of the total hydrogen peroxide formation rate $V_{3,7}(\text{H}_2\text{O}_2)$ on the dissolved oxygen concentration x from empirical data (symbols) using Eqs. (3a) and (12) with $\beta = 0$ (model optimization with respect to the parameter α) for the γ -radiolysis of water saturated with hydrogen and containing different amounts of oxygen at 296 K [63] ($S_\gamma = 1.13 \times 10^{-8}$). The dashed curve described $V_3(\text{H}_2\text{O}_2)$ as a function of the oxygen concentration x based on Eq. (3a) (model optimization with respect to α) and the experimental data of curve 2 ($S_\gamma = 1.73 \times 10^{-8}$).

ii. Addition of the Hydrogen Atom

A number of experimental findings concerning the autoinhibiting effect of an increasing oxygen concentration at modest temperatures on hydrogen oxidation both in the gas phase [47,64,65] (Fig. 4) and in the liquid phase [63] (Fig. 3, curve 2), considered in our earlier work [66], can also be explained in terms of the competition kinetics of free radical addition [14,67].

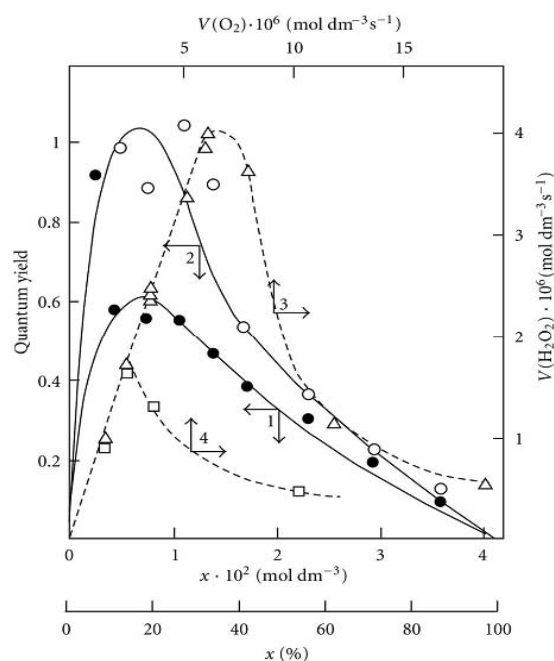


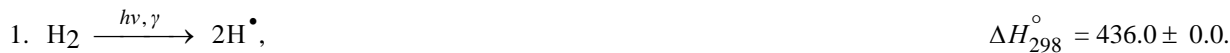
Fig. 4 : (1, 2) Quantum yields of (1, \bullet) hydrogen peroxide and (2, \circ) water resulting from the photochemical oxidation of hydrogen in the hydrogen–oxygen system as a function of the oxygen concentration x (light wavelength of 171.9–172.5 nm, total pressure of 10^5 Pa, room temperature [64]). (3, 4) Hydrogen peroxide formation rate $V(\text{H}_2\text{O}_2)$ (dashed curves) as a function of the rate $V(\text{H}_2\text{O}_2)$ at which molecular oxygen is passed through a gas-discharge tube filled with (3, Δ) atomic and (4, \square) molecular hydrogen. Atomic hydrogen was obtained from molecular hydrogen in the gas-discharge tube before the measurements (total pressure of 25–77 Pa, temperature of 77 K [47]). The symbols represent experimental data.

Scheme 4

Nonbranched-chain oxidation of hydrogen and changes in enthalpy (ΔH_{298}° , kJ mol^{-1}) for elementary reactions⁹

⁹According to Francisco and Williams [49], the enthalpy of formation (ΔH_f°) in the gas phase of H^\bullet , HO^\bullet , HO_2^\bullet , HO_4^\bullet (the latter without the possible intramolecular hydrogen bond taken into account), O_3 , H_2O [2], H_2O_2 , and H_2O_4 is 218.0 ± 0.0 , 39.0 ± 1.2 , 12.6 ± 1.7 , 122.6 ± 13.7 , 143.1 ± 1.7 , -241.8 ± 0.0 , -136.0 ± 0 , and $-26.0 \pm 9 \text{ kJ mol}^{-1}$, respectively. Calculations for the $\cdot\text{HO}_4$ radical with a helical structure were carried out using the $\text{G}_2(\text{MP}_2)$ method [68]. The stabilization energies of HO_2^\bullet , HO_4^\bullet , and HO_3^\bullet were calculated in the same work to be 64.5 ± 0.1 , 69.5 ± 0.8 , and $88.5 \pm 0.8 \text{ kJ mol}^{-1}$, respectively. The types of the O_4 molecular dimers, their IR spectra, and higher oxygen oligomers were reported [69,70]. The structure and IR spectrum of the hypothetical cyclotetraoxygen molecule O_4 , a species with a high energy density, were calculated by the CCSD method, and its enthalpy of formation was estimated [71]. The photochemical properties of O_4 and the van der Waals nature of the O_2 – O_2 bond were investigated [72,73]. The most stable geometry of the dimer is two O_2 molecules parallel to one another. The O_4 molecule was identified by NR mass spectrometry [74].

Chain initiation



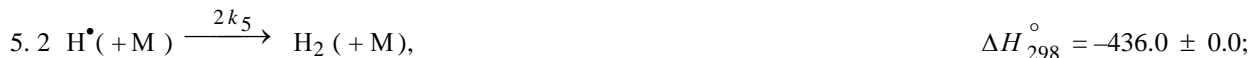
Chain propagation



Inhibition



Chain termination



The hydroperoxyl free radical HO_2^\bullet [75–78] resulting from reaction (2) possesses an increased energy due to the energy released the conversion of the $\text{O}=\text{O}$ multiple bond into an $\text{HO}-\text{O}^\bullet$ ordinary bond. Therefore, before its possible decomposition, it can interact with a hydrogen or oxygen molecule as the third body *via* parallel (competing) reactions (3) and (4), respectively. The hydroxyl radical HO^\bullet that appears and disappears in consecutive parallel reactions (3) (first variant) and 3' possesses additional energy owing to the exothermicity of the first variant of reaction 3, whose heat is distributed between the two products. As a consequence, this radical has a sufficiently high reactivity not to accumulate in the system during these reactions, whose rates are equal ($V_3 = V_{3'}$) under quasi-steady-state conditions, according to the above scheme. Parallel reactions 3 (second, parenthesized

variant) and 3' regenerate hydrogen atoms. It is assumed [56,57] that the hydrotetraoxyl radical HO_4^\bullet (first reported in [79,80]) resulting from endothermic reaction 4, which is responsible for the peak in the experimental rate curve (Fig. 2, curve 3), is closed into a five-membered $[\text{OO}-\text{H}\cdots\text{O}]^\bullet$ cycle due to weak intramolecular hydrogen bonding [54,81]. This structure imparts additional stability to this radical and makes it least reactive.

The HO_4^\bullet radical was discovered by Staehelin *et al.* [82] in a pulsed γ -radiolysis study of ozone degradation in water; its UV spectrum with an absorption maximum at 260 nm ($\epsilon(\text{HO}_4^\bullet)_{260 \text{ nm}} = 320 \pm 15 \text{ m}^2 \text{ mol}^{-1}$) was reported. The spectrum of the HO_4^\bullet radical is similar to that of ozone, but the molar absorption coefficient $\epsilon(\text{HO}_4^\bullet)_{\lambda \text{ max}}$ of the former is almost two times larger [82]. The assumption about the cyclic

structure of the HO_4^\bullet radical can stem from the fact that its mean lifetime in water at 294 K, which is $(3.6 \pm 0.4) \times 10^{-5}$ s (as estimated [66] from the value of $1/k$ for the reaction $\text{HO}_4^\bullet \xrightarrow{k} \text{HO}_2^\bullet + \text{O}_2$ [82]), is 3.9 times longer than that of the linear HO_3^\bullet radical [68, 83] estimated in the same way [66] for the same conditions [84], $(9.1 \pm 0.9) \times 10^{-6}$ s. MP2/6-311++G** calculations using the Gaussian-98 program confirmed that the cyclic structure of HO_4^\bullet [85] is energetically more favorable than the helical structure [68] (the difference in energy is 4.8–7.3 kJ mol⁻¹, depending on the computational method and the basis set).¹⁰ For example, with the MP2(full)/6-31G(d) method, the difference between the full energies of the cyclic and acyclic HO_4^\bullet conformers with their zero-point energies (ZPE) values taken into account (which reduces the energy difference by 1.1 kJ mol⁻¹) is -5.1 kJ mol⁻¹ and the entropy of the acyclic-to-cyclic HO_4^\bullet transition is $\Delta S_{298}^\circ = -1.6$ kJ mol⁻¹ K⁻¹. Therefore, under standard conditions, HO_4^\bullet can exist in both forms, but the cyclic structure is obviously dominant (87%, $K_{\text{eq}} = 6.5$) [85].

Reaction (4) and, to a much lesser degree, reaction (6) inhibit the chain process, because they lead to inefficient consumption of its main participants – HO_2^\bullet and H^\bullet .

The hydrogen molecule that results from reaction (5) in the gas bulk possesses an excess energy, and, to acquire stability within the approximation used in this work, it should have time for deactivation *via* collision with a particle M capable of accepting the excess energy [87]. To simplify the form of the kinetic equations, it was assumed that the rate of the bimolecular deactivation of the molecule substantially exceeds the rate of its monomolecular decomposition, which is the reverse of reaction 5 [2].

Reactions 6 and 7 (taking into account the principle of detailed balance for the various pathways) regenerate hydrogen and oxygen (in the form of $\text{O}_2(X^3\Sigma_g^-)$ molecules, including the singlet states with $\Delta H_{f298}^\circ(\text{O}_2,$

$a^1\Delta_g) = 94.3$ kJ mol⁻¹[20, 41] and $\Delta H_{f298}^\circ(\text{O}_2, b^1\Sigma_g^+) = 161.4$ kJ mol⁻¹[41], which are deactivated by collisions, and in the form of O_3) and yield hydrogen peroxide or water *via* a nonchain mechanism, presumably through the intermediate formation of the unstable hydrogen tetraoxide molecule H_2O_4 [61, 62].¹⁰ Ozone does not interact with molecular hydrogen. At moderate temperatures, it decomposes fairly slowly, particularly in the presence of $\text{O}_2(X^3\Sigma_g^-)$ [41]. The reaction of ozone with H^\bullet atoms, which is not impossible, results in their replacement with HO^\bullet radicals. The relative contributions from reactions 6 and 7 to the process kinetics can be roughly estimated from the corresponding enthalpy increments (*Scheme 2*).

When there is no excess hydrogen in the hydrogen–oxygen system and the homomolecular dimer O_4 [71–74,89,90], which exists at low concentrations (depending on the pressure and temperature) in equilibrium with O_2 [70], can directly capture the H^\bullet atom to yield the heteronuclear cluster HO_4^\bullet ,¹² which is more stable than O_4 [70] and cannot abstract a hydrogen atom from the hydrogen molecule, nonchain hydrogen oxidation will occur to give molecular oxidation products *via* the disproportionation of free radicals.

The low-reactive hydrotetraoxyl radical HO_4^\bullet [82], which presumably has a high energy density [71], may be an intermediate in the efficient absorption and conversion of biologically hazardous UV radiation energy the Earth upper atmosphere. The potential energy surface for the atmospheric reaction $\text{HO}^\bullet + \text{O}_3$, in which the adduct $\text{HO}_4^\bullet(^2A)$ was considered as an intermediate, was calculated by the DMBE method [91]. From this standpoint, the following reactions are possible in the upper troposphere, as well as in the lower and middle stratosphere, where most of the ozone layer is situated (altitude of 16–30 km, temperature of 217–227 K, pressure of 1.0×10^4 – 1.2×10^3 Pa [92]; the corresponding ΔH_{298}° reaction values are given in kJ mol⁻¹ [49]):



¹⁰There were calculations for the two conformers (*cis* and *trans*) of the HO_4^\bullet radical [86] using large scale *ab initio* methods and density functional techniques with extended basis sets. Both conformers have a nearly planar geometry with respect to the four oxygen atoms and present an unusually long central O–O bond. The most stable conformer of HO_4^\bullet radical is the *cis* one, which is computed to be endothermic with respect to $\text{HO}_2^\bullet(X^2A'') + \text{O}_2(X^3\Sigma_g^-)$ at 0 K.

¹¹The planar, six-atom, cyclic, hydrogen-bonded dimer $(\text{HO}_2^\bullet)_2$ was calculated using quantum chemical methods (B3LYP density functional theory) [88]. The hydrogen bond energy is 47.7 and 49.4 kJ mol⁻¹ at 298 K for the triplet and singlet states of the dimer, respectively.

¹²It is impossible to make a sharp distinction between the two-step bimolecular interaction of three species *via* the equilibrium formation of the labile intermediate O_4 and the elementary termolecular reaction $\text{O}_2 + \text{O}_2 + \text{H}^\bullet \rightarrow \text{HO}_4^\bullet$.

The HO₄[•] radical can disappear *via* disproportionation with a molecule, free radical, or atom in addition to dissociation. Note that emission from O₂ (a¹Δ_g) and O₂(b¹Σ_g⁺) is observed at altitudes of 30–80 and 40–130 km, respectively [93].

Staehelin *et al.* [82] pointed out that, in natural systems in which the concentrations of intermediates are often very low, kinetic chains in chain reactions can be very long in the absence of scavengers since the rates of the chain termination reactions decrease with decreasing concentrations of the intermediates according to a quadratic law, whereas the rates of the chain propagation reactions decrease according to a linear law.

The kinetic description of the noncatalytic oxidation of hydrogen, including in an inert medium [87], in terms of the simplified scheme of free-radical nonbranched chain reactions (*Scheme 4*), which considers only quadratic-law chain termination and ignores the surface effects [47], at moderate temperatures and pressures, in the absence of transitions to unsteady-state critical regimes, and at a substantial excess of the hydrogen concentration over the oxygen concentration was obtained by means of quasi-steady-state treatment, as in the previous studies on the kinetics of the branched-chain free-radical oxidation of hydrogen [76], even though the applicability of this method in the latter case under unsteady states conditions was insufficiently substantiated. The method was used with the following condition:¹³ $k_6 = \sqrt{2k_5 2k_7}$ (see Introduction). The equation for the rate of the chain formation of hydrogen peroxide and water, $V_3(\text{H}_2\text{O}_2; \text{H}_2\text{O}) = V_3'(\text{H}_2\text{O})$, *via* reactions 3 and 3' is identical to Eq. (3, 3a) with the corresponding analytical expression for k_2 . The ratio of the rates of the competing reactions is $V_3/V_4 = \alpha l/x$, and the chain length is $\nu = V_3/V_1$. The rates of nonchain formation of hydrogen peroxide and water *via* reactions (6) and (7) – quadratic-law chain termination - are identical to Eqs. (11) and (12) provided that $\beta = 0$. In these equations, l and x are the molar concentrations of hydrogen and oxygen ($l \gg x$), l_m and x_m are the respective concentrations at the maximum point of the function, V_1 is the rate of initiation (reaction 1), $\alpha = k_3/k_4$, the rate constant $k_2 = \alpha l_m \sqrt{2k_5 V_1} / x_m^2$ is derived from the condition $\partial V_3/\partial x = 0$, and $2k_5$ is the rate constant of reaction 5 (hydrogen atom recombination), which is considered as bimolecular within the given approximation.¹⁴

In the case of nonchain hydrogen oxidation *via* the above addition reaction ($\text{H}^\bullet + \text{O}_4 \xrightarrow{k_{add}} \text{HO}_4^\bullet$), the formation rates of the molecular oxidation products in reactions 6 and 7 (*Scheme 4*, $k_2 = k_3 = k_4 = 0$) are defined by modified Eqs. (11) and (12) in which $\beta = 0$, ($\alpha l + x$) is replaced with 1, and k_2 is replaced with $k_{add}K_{eq}$ ($k_{add}K_{eq}$ is the effective rate constant of H[•] addition to the

O₄ dimer, $K_{eq} = k/k'$ is the equilibrium constant of the reversible reaction $2\text{O}_2 \xrightleftharpoons[k']{k} \text{O}_4$ with $k' \gg k_{add}[\text{H}^\bullet]$). The formation rates of the stable products of nonchain oxidation ($k_3 = 0$), provided that either reactions (2) and (4) or reaction (2) alone ($k_4 = 0$) occurs (*Scheme 4*; in the latter case, reactions 6 and 7 involve the HO₂[•] radical rather than HO₄[•]), are given by modified Eqs. (11) and (12) with $\beta = 0$, ($\alpha l + x$) replaced with 1, and x^2 replaced with x .

Note that, if in *Scheme 4* chain initiation *via* reaction 1 is due to the interaction between molecular hydrogen and molecular oxygen yielding the hydroxyl radical HO[•] in stead of H[•] atoms and if this radical reacts with an oxygen molecule (reaction 4) to form the hydrotrioxyl radical HO₃[•] (which was obtained in the gas phase by neutralization reionization (NR) mass spectrometry [83] and has a lifetime of $>10^{-6}$ s at 298 K) and chain termination takes place *via* reactions 5–7 involving the HO[•] and HO₃[•], radicals instead of H[•] and HO₄[•], respectively, the expressions for the water chain formation rates derived in the same way will appear as a rational function of the oxygen concentration x without a maximum: $V_3'(\text{H}_2\text{O}) = V_1 k_3 l (K_4 x + \sqrt{2k_5 V_1})$.

Curve 2 in Fig. 3 describes, in terms of the overall equation $V_{3,7} = V_1 x (\alpha l f_m + x^3) f_m^2$ for the rates of reactions 3 and 7 (which was derived from Eqs. 3a and 12, respectively, the latter in the form of $V_7 = V_1 x^4 / f_m^2$ (12a) [96] in which k_2 is replaced with its analytical expression derived from Eq. (8) with $\beta = 0$ everywhere), the dependence of the hydrogen peroxide formation rate (minus the rate $V_{\text{H}_2\text{O}_2} = 5.19 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$ of the primary formation of hydrogen peroxide after completion of the reactions in spurs) on the initial concentration of dissolved oxygen during the γ -radiolysis of water saturated with hydrogen ($7 \times 10^{-4} \text{ mol dm}^{-3}$) at 296 K [63]. These data were calculated in the present work from the initial slopes of hydrogen peroxide buildup versus dose curves for a ⁶⁰Co γ -radiation dose rate of $P = 0.67 \text{ Gy s}^{-1}$ and absorbed doses of $D \cong 22.5\text{--}304.0 \text{ Gy}$. The following values of the

¹³For example, the ratio of the rate constants of the bimolecular disproportionation and dimerization of free radicals at room temperature is $k(\text{HO}^\bullet + \text{HO}_2^\bullet) / [2k(2\text{HO}^\bullet)2k(2\text{HO}_2^\bullet)]^{0.5} = 2.8$ in the atmosphere [92] and $k(\text{H}^\bullet + \text{HO}^\bullet) / [2k(2\text{H}^\bullet)2k(2\text{HO}^\bullet)]^{0.5} = 1.5$ in water [94]. These values that are fairly close to unity.

¹⁴This rate constant in the case of the pulsed γ -radiolysis of ammonia-oxygen (+ argon) gaseous mixtures at a total pressure of 10^5 Pa and a temperature of 349 K was calculated to be $1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [65] (a similar value of this constant for the gas phase was reported in an earlier publication [95]). Pagsberg *et al.* [65] found that the dependence of the yield of the intermediate HO[•] on the oxygen concentration has a maximum close to $5 \times 10^{-4} \text{ mol dm}^{-3}$. In the computer simulation of the process, they considered the strongly exothermic reaction $\text{HO}_2^\bullet + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NHOH}$, which is similar to reaction 3 in *Scheme 4*, whereas the competing reaction 4 was not taken into account.

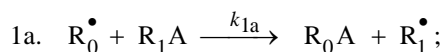
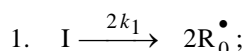
primary radiationchemical yield G (species per 100 eV of energy absorbed) for water γ -radiolysis products in the bulk of solution at pH 4–9 and room temperature were used (taking into account that $V = GP$ and $V_1 = G_H P$): $G_{H_2O_2} = 0.75$ and $G_H = 0.6$ (initiation yield; see Conclusions) [94]; $V_1 = 4.15 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$; $2k_5 = 2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [94]. As can be seen from Fig. 3, the best description of the data with an increase in the oxygen concentration in water is attained when the rate V_7 of the formation of hydrogen peroxide *via* the nonchain mechanism in the chain termination reaction 7 (curve 1, $\alpha = (8.5 \pm 2) \times 10^{-2}$) is taken into account in addition to the rate V_3 of the chain formation of this product *via* the propagation reaction 3 (dashed curve 2, $\alpha = 0.11 \pm 0.026$). The rate constant of addition reaction 2 determined from α is substantially underestimated: $k_2 = 1.34 \times 10^7$ (vs 2.0×10^{10} [94]) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The difference can be due to the fact that the radiation-chemical specifics of the process were not considered in the kinetic description of the experimental data. These include oxygen consumption *via* reactions that are not involved in the hydrogen oxidation scheme [66,97,98] and reverse reactions resulting in the decomposition of hydrogen peroxide by intermediate products of water γ -radiolysis (e_{aq}^- , H^\bullet , HO^\bullet), with the major role played by the hydrated electron e_{aq}^- [94].

d) *General Scheme of the Free-Radical Addition to Olefins, Formaldehyde, and Oxygen*

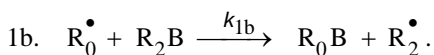
The general scheme of the nonbranched-chain addition of a free radical from a saturated compound to an olefin (and its functionalized derivative), formaldehyde, or dioxygen in liquid homogeneous binary systems of these components includes the following reactions [57,97,98].

Scheme 5

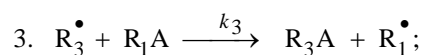
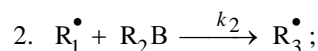
Initiation



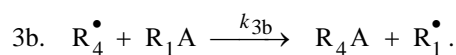
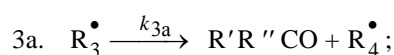
for addition to an olefin at comparable component concentrations,



Chain propagation

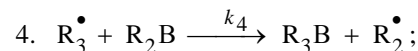


for addition to O_2 and the 1-hydroxyalkyl radical to CH_2O ,

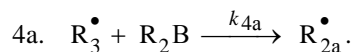


Inhibition

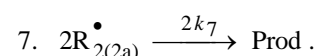
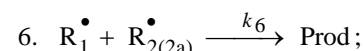
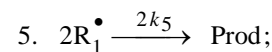
For addition to an olefin or CH_2O ,



for addition to O_2 ,



Chain termination



In this scheme, I is the initiator, for example, a peroxide [5,17,18,29,30]; R_0^\bullet is any reactive radical (initiator); A is an atom of hydrogen [2,5,6,17,18,22–24,29–32] or halogen [2,5,19–21]; B is an atom of hydrogen [5,17–21,23,24,29–32], halogen [22], or oxygen (in oxidation) [2,5,6,16,44–46]; R_1^\bullet is a radical such as $^\bullet PCl_2$ [19], $^\bullet CCl_3$ [20], an alkyl [2,5,6,21], a 1-hydroxyalkyl [5,6,17,22–24,29,32], or a similar functionalized radical [5] (addend); R_2^\bullet is the formyl [8,9,29], an alkenyl (propenyl or higher) [2,5,17–22], a 1-hydroxyalkenyl [5,17,18,23,24], or a similar functionalized low-reactive radical [5,18] (inhibitor) or the oxygen atom (in oxidation) [2,5,6,13,14,16,44–46,56,57,96–98]; R_{2a}^\bullet is the low-reactive alkyltetraoxyl 1:2 adduct radical RO_4^\bullet [13,14,56,57,96–98] (inhibitor); R_3^\bullet is the active 1:1 adduct radical; R_4^\bullet is an active fragment radical, such as hydroxymethyl [8,9,12,29,32], an alkoxy radical, or hydroxyl (in oxidation) [2,5,6,13,14,16,44,46,56,57,96–98]; R_0A , R_0B , R_1A , and R_4A are saturated molecules; R_2B is an unsaturated molecule, viz., an olefin [2,5,11,17–22], formaldehyde [8,9,12,29–32], or dioxygen (in oxidation) [2,5,6,13,14,16,44–46,56,57,96–98]; $R'R''CO$ is a carbonyl compound viz., aldehyde [2,6,8,9,12,14,29–32,44] or ketone [2,6,14,29,32,44]; R_3A and R_3B are molecular products (1:1 adducts); and Prod stands for molecular products of the dimerization and disproportionation of free radicals.

The chain evolution stage of *Scheme 5* include consecutive reactions 2, 3; 2, 3a; and 3a, 3b; parallel (competitive) reactions 3, 3a; 3, 3b; 3, 4 (or 4a); and 3a, 4 (or 4a); and consecutive-parallel reactions 2 and 4 (or 4a). Addition to olefins is described by reactions 1–3, 4, and 5–7 and the corresponding rate equations (1)–(4a). Addition to the carbonyl carbon atom of the free (unsolvated) form of formaldehyde is represented by reactions 1, 1a, 2–4 (the main products are a 1,2-

alkanediol, a carbonyl compound, and methanol), and 5–7 and is described by Eqs. (5) and (6). In the case of hydroxymethyl addition, the process includes reactions 1, 1a, 2, 3, 5a, 4 (the main product is ethanediol), and 5–7 and is described by Eq. (7). If the nonchain formation of ethanediol in reaction 5 is ignored, the process is described by Eq. (5). Addition to the oxygen molecule is described by reactions 1, 1a, 2–3b, 4a (the main products are an alkyl hydroperoxide, alcohols, carbonyl compounds, and water), and 5–7 and Eqs. (8), (8a), (9), and (9a).

The main molecular products of the chain process – R_3A , $R'R''CO$, and R_4A – result from reactions 3, 3a, and 3b – chain propagation through the reactive free radical R_1^* or R_2^* , $R'R''CO$. The competing reaction 4, which opposes this chain propagation, yields the by-product R_3B a nonchain mechanism. The rate of formation of the products is a complicated function of the formation rates ($V_{3a} = V_{3b}$) and disappearance rates of the free radicals R_1^* and R_2^* : $V(R_3A, R'R''CO, R_4A, R_3B) = V_2 = V_3 + V_{3a} + V_{4(4a)} = (V_{1a} + V_3 + V_{3b} - V_5) - (V_{1b} + V_{4(4a)} - V_7)$. The rates of reactions 5–7 at $k_{1b} = 0$ ($[R_1A] \gg [R_2B]$) are given by Eqs. (9)–(11). The rate ratios of the competing reactions are $V_3/V_{4(4a)} = \alpha/x$ and $V_{3a}/V_{4(4a)} = \beta/x$ (where $\alpha = k_3/k_{4(4a)}$, $\beta = k_{3a}/k_{4(4a)}$ mol dm⁻³, and l and x are the molar concentrations of the reactants R_1A and R_2B , respectively), and the chain length is $\nu = (V_3 + V_{3a})/V_1$. Unlike the dependences of the rates of reactions 4a (or 4 at $k_{1b} = 0$, with $V_{4(4a)} \leq V_1$), 5, and 7 (Eqs. (9), (10), and (12)), the dependences of the rates V of reactions 3, 3a,b, 4 (at $k_{1b} \neq 0$), and 6 (Eqs. (1)–(9a) and (11)) on x have a maximum. Reaction 1b, which competes with reaction 1a, gives rise to a maximum in the dependence described by Eq. (2), whereas reaction 4 or 4a, competing with reactions 3 and 3a,b, is responsible for the maxima in the dependences defined by Eqs. (1), (3)–(7) or (8, 8a) and (9, 9a). The low-reactive radicals R_2^{*15} and R_{2a}^* , resulting from reactions 4 and 4a, inhibit the nonbranched-chain addition of R_1^* to olefins (or formaldehyde) and dioxygen, respectively. Reaction 4a leads to non-productive loss of R_3^* adduct radicals.

For approximate estimation of the parameters of the kinetic equations (3), (4), (8), and (9), Eq. (4) under the conditions (a) $k_2x^2 \ll (\alpha + x)\sqrt{2k_5V_1}$ (ascending branch of a peaked curve) and (b) $k_2x^2 \gg (\alpha + x)\sqrt{2k_5V_1}$ (descending branch) is transformed into simple functions (direct and inverse proportionality, respectively) of the concentration x of the unsaturated compound. These functions allow tentative estimates of the parameters k_2 and α to be derived from the experimental product formation rate V provided that V_1 and $2k_5$ are known:

$$V_{3,4} = \sqrt{V_1 k_2 x / \varphi} \sqrt{2k_5} \quad (13)$$

$$V_{3,4} = (V_1/\varphi)[(\alpha/x) + 1], \quad (14)$$

where $\varphi = 1$ under conditions (a) and (b) and $\varphi = 2$ at the point of maximum (where $k_2x^2 \cong (\alpha + x)\sqrt{2k_5V_1}$). Equations (8) and (9) under the condition $k_2x^2 \gg (\alpha + \beta + x)\sqrt{2k_5V_1}$ (descending branch of a peaked curve) can be transformed into Eqs. (15) and (16), respectively, which express the simple, inversely proportional dependences of reaction rates on x and provide tentative estimates of α and β :

$$V_3 = V_1 \alpha l / \varphi x, \quad (15)$$

$$V_{3a} = V_1 \beta / \varphi x, \quad (16)$$

where $\varphi = 2$ at the point of maximum (where $k_2x^2 \cong (\alpha + \beta + x)\sqrt{2k_5V_1}$) and $\varphi = 1$ for the descending branch of the curve. Equation (3) for $V_{3,4}$ under condition (b) transforms into Eq. (15).

For radiation-chemical processes, the rates V in the kinetic equations should be replaced with radiation-chemical yields G using the necessary unit conversion factors and the relationships $V = GP$ and $V_1 = \varepsilon_1 G(R_1^*)P$, where P is the dose rate, ε_1 is the electron fraction of the saturated component R_1A in the reaction system [100], and $G(R_1^*)$ is the initial yield of the chain-carrier free radicals (addends) – initiation yield [39,94].

The optimum concentration of the unsaturated component in the system maximizing the process rate, x_m , can be calculated using rate equations (3a), (4a), (8a), and (9a) or the corresponding analytical expressions for k_2 provided that the other parameters involved in these equations are known. This opens up the way to intensification of some technological processes that are based on the addition of free radicals to C=C, C=O, and O=O bonds and occur via a nonbranched-chain mechanism through the formation of a 1:1 adduct.

II. CONCLUSIONS

The above data concerning the competition kinetics of the nonbranched-chain addition of saturated free radicals to the multiple bonds of olefins (and its derivatives), formaldehyde, and oxygen molecules make it possible to describe, using rate equations (1)–(9a), obtained by quasi-steady-state treatment, the peaking experimental dependences of the formation rates of molecular 1:1 adducts on the initial concentration of the unsaturated compound over the entire range of its variation in binary systems consisting of saturated and unsaturated components (Figs. 1–3). In such reaction

¹⁵The stabilization energy of the low-reactive free radicals $CH_2=C(CH_3)\dot{C}H_2$, $CH_2=CH\dot{C}HOH$, and $H\dot{C}=O$ in the standard state in the gas phase is –52.0, –42.1, and –24.3 kJ mol⁻¹, respectively [4,99].

systems, the unsaturated compound is both a reactant and an autoinhibitor, specifically, a source of low-reactive free radicals shortening kinetic chains. The progressive inhibition of the nonbranched-chain processes, which takes place as the concentration of the unsaturated compound is raised (after the maximum process rate is reached), can be an element of the self-regulation of the natural processes that returns them to the stable steady state.

A similar description is applicable to the nonbranched-chain free-radical hydrogen oxidation in water at 296 K [63] (Fig. 3, curve 2). Using the hydrogen oxidation mechanism considered here, it has been demonstrated that, in the Earth's upper atmosphere, the decomposition of O₃ in its reaction with the HO• radical can occur via the addition of the latter to the ozone molecule, yielding the HO•₄ radical, which is capable of efficiently absorbing UV radiation [82].

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A Dispersive Liquid - Liquid Microextraction based Gas Chromatography-Mass Spectrometry (DLLME-GC-MS) Method for the Simultaneous Determination of Fungicide Residues in Fruit Samples

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Abstract - A simple and sensitive dispersive liquid – liquid microextraction method based gas chromatography mass spectrometry (DLLME-GC-MS) has been developed for the simultaneous determination of twelve azole fungicides (Tetraconazole, Penconazole, Tricyclazole, Propiconazole, Tebuconazole, Epoxyconazole, Etoxadazole, Fluquinconazole, Difenconazole) in fruit samples. The following parameters that affect the DLLME procedure efficiency were optimized: Selection of extraction solvent and dispersion solvent, extraction time and ionic strength. Under the optimal conditions the linearity of the method was established over the range 0.001 – 1.0 µg/mL with the correlation coefficients ranging from 0.9962 – 0.9997. The recoveries of the DLLME ranged from 85 to 105, with relative standard deviation (RSD) < 9.5%.

Keywords : *dispersive liquid-liquid microextraction, fungicides, fruits, gas chromatograph, mass spectrometer.*

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A Dispersive Liquid- Liquid Microextraction based Gas Chromatography - Mass Spectrometry (DLLME-GC-MS) Method for the Simultaneous Determination of Fungicide Residues in Fruit Samples

Thammisetty Venkata Rao^α, Gundodju Suresh^ο & Atmakuru Ramesh^ρ

Abstract - A simple and sensitive dispersive liquid - liquid microextraction method based gas chromatography mass spectrometry (DLLME-GC-MS) has been developed for the simultaneous determination of twelve azole fungicides (Tetraconazole, Penconazole, Tricyclazole, Propiconazole, Tebuconazole, Epoxyconazole, Etoxazole, Fluquinconazole, Difenconazole) in fruit samples. The following parameters that affect the DLLME procedure efficiency were optimized: Selection of extraction solvent and dispersion solvent, extraction time and ionic strength. Under the optimal conditions the linearity of the method was established over the range 0.001 – 1.0 µg/mL with the correlation coefficients ranging from 0.9962 – 0.9997. The recoveries of the DLLME ranged from 85 to 105, with relative standard deviation (RSD) < 9.5%. The developed and optimized method was applied successfully for the determination of residues in market fruit samples.

Keywords : *dispersive liquid-liquid microextraction, fungicides, fruits, gas chromatograph, mass spectrometer.*

I. INTRODUCTION

Nowadays, a large group of fungicides have been introduced in agriculture for the control and the prevention of diseases their by protecting the quantity and quality of agricultural products. Fungicides are sprayed directly on fruits and leaves to prevent the attack of fungi, which reduce the yield of fruit [1]. Some of these fungicides are used for stabilizing fruit during the storage and transport process. Monitoring of the residues in fruits at trace levels is a global regulatory demand as part of environmental safety controls and public health protection.

The crop matrixes are complex and involves extensive procedures to monitor the trace levels of residues. Lower the detection the lower the ruggedness in extraction and measurements.

There are several methods that describe the multi residue detection of fungicides in fruit samples. Majority of the methods are very specific and suffers from their adoptability to other crops. Sample preparation and extraction plays a major role in the field of pesticide residue analysis. Solid phase extraction (SPE) is the most common method for extraction of fungicides residues [2, 3]. The SPE technique is time consuming, cost effect and labor-expensive. Apart from SPE, the Solid Phase Micro Extraction (SPME) was also applied to the determination of several fungicides [4-6]. The SPME normally provides a higher selectivity than SPE the matrix of samples reduces significantly its extraction efficiency [7, 8]. Some of these drawbacks have been overcome by the DLLME technique was first introduced by Assadi et al, [9]. This method consists of two steps. The first is injection of an appropriate mixture of extraction and dispersion solvent into aqueous sample as very fine droplets and analytes were enriched into it. Because of the infinitely large surface area between extractions solvent and aqueous sample the equilibrium state was achieved quickly and extraction was independent of time. The second step is the centrifugation of cloudy solution. After centrifugation, the determination of analytes in sediment phase can be performed by instrumental analysis. Consequently, high enrichment factor simplicity of operation and low cost are some of the advantaged of this method. Some of published reports indicates the extraction of pesticide from fruit samples using DLLME procedure [10-13]. However not much work was reported in determination of azole group of fungicides in fruit samples by DLLME. In this study 12 azole fungicides (Tetraconazole, Penconazole, Tricyclazole, Propiconazole, Tebuconazole, Epoxyconazole, Etoxazole, Fluquinconazole, Difenconazole) were studied in fruit samples. The aim of the present work was to develop and validate the simultaneous determination azoles in three kinds of fruits using DLLME-GC-MS. In addition the effects of different parameters on the efficiency of DLLME method were investigated. The advantage of DLLME method is

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its limited use of solvent which is environmental friendly and requires less time and minimal amount of solvent. This environment friendly technique is safe and effective and analytical friendly, once extracted the sample can be directly used without any further clean for the quantification of residues and can also be directly introduced in to the head space injector port.

II. MATERIALS AND METHODS

a) Chemicals and Reagents

Standards of Tetraconazole (purity-98.9%), Penco-nazole (purity-98.9%), Tricyclazole (purity-98.9%), Propi-conazole (purity-98.9%), Tebuconazole (purity-98.9%), Epoxyconazole (purity-98.9%), Etoxazole (purity-98.9%), Fluquinconazole (purity-98.9%), Difenconazole (purity-98.9%) were purchased from sigma Aldrich, USA.

Extraction solvents, chlorobenzene (C₆H₅Cl), carbon tetrachloride (CCl₄), tetrachloro ethane (C₂H₂Cl₄), Chloroform (CHCl₃), were purchased from Merck (Merck, Mumbai). Disperser solvents, acetone, acetonitrile, tetrahydrofuran and methanol were obtained from Sigma Aldrich. The water used was ultrapure (Millipore Unit). Sodium chloride (NaCl), was purchased from Merck Chemicals.

b) Instrumentation and GC-MS Conditions

GC-MS analyses was performed using Shimadzu GC MS-QP5000 (Shimadzu, Japan). The HP-1 MS capillary column (30m x 0.25mm i.d with 0.1 μm film thickness) was used for separation. Injection was carried out in the split mode (5:1) at an injector temperature of 290°C. Helium gas was used as a carrier gas with a flow rate of 1.0 mL/min. The column temperature was maintained at 160°C for 13 min and then programmed at 10°C min⁻¹ to 200°C for 5 min followed by a final ramp to 290°C at a rate of 50°C min⁻¹, and held for 6min. The ion source and transfer line temperature was 300°C respectively. All the samples were analysed in Electron Impact Ionization (EI) mode.

c) Method Validation

Specificity, linearity and recovery studies were conducted by injecting the al control samples. Different know concentrations of linearity solutions 1.0, 0.5, 0.1, 0.01, 0.005 and 0.001 μg/mL were prepared by serial dilutions method using acetone and injected in GC-MS. The limit of determination (LOD) was determined as 0.001 μg/mL based on signal noise ratio 3:1. A calibration curve was plotted between the peak area and concentration of the analytes.

Recovery studies in fruit samples were conducted by fortifying different concentrations of standard solutions (0.005 μg/g and 0.05 μg/g) of analytes.

For the repeatability analysis, five replicated determinations were made at each concentration level. After fortification of standards, the samples were

homogenized as per extraction procedure and analysed GC-MS. The method has a limit of quantification (LOQ) 0.005 μg/mL. The RSD% for each concentration was calculated.

d) Sample Pretreatment Procedure

The representative sample (200 g of fruit) was homogenized by miller. A 20 g of homogenized sample was weighed and transferred into a centrifuge tubes. The sample was centrifuged for 5 minutes at 15,000 RPM using REMI cooling centrifuge. The supernant was filtered through 0.45μm PTFE Nylon filter into 10-mL volumetric flask with doubly distilled water to the volume for the DLLME procedure.

e) Extraction Procedure - DLLME

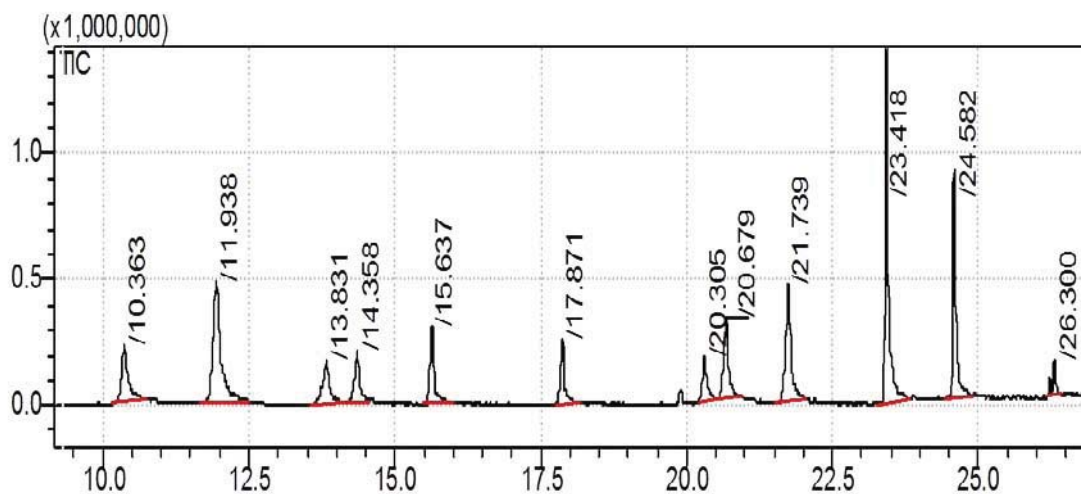
A 5.0 mL of fruit sample solution previously obtained was placed into a 10.0 mL glass vial with conical bottom and 1% (w/v) of sodium chloride (NaCl) was added to the glass vial. The organic solution containing 0.7 mL acetonitrile as dispersive solvent and 15.0 μL C₂H₂Cl₄ as extraction solvent was rapidly injected into the sample solution. Then the sample solution was gently shaken for 30 sec, and a cloudy solution was formed in the glass vial. In this step the analytes in sample solution were extracted into the fine droplets of C₂H₂Cl₄ rapidly.

In order to separate the organic phase from the aqueous phase the sample was centrifuged for 5 min at 3,500 RPM. After this process, the dispersed fine droplets of C₂H₂Cl₄ were sedimented at the bottom of the glass vial. The sedimented phase (8±0.5 μL) was transferred in to sample vial and 1 μL of sedimented phase was injected to GC-MS for analysis.

III. RESULT AND DISCUSSION

a) Analytical Data- Linearity, Recovery and Repetability

The method was found to linear with a correlation coefficient of 0.9962 – 0.9997 when the tested in the range 0.001 to 1.0 μg/mL. The limit of determination (LOD) was determined as 0.001 μg/mL based on signal noise ratio 3:1. The method has a limit of quantification (LOQ) 0.005 μg/mL. The recovery details are presented in Table 2.



S.No.	Name of the Compound	Retention Time (min)	Molecular Mass (m/Z)
1	Tetraconazole	10.3	372.2
2	Penconazole	11.9	284.2
3	Tricyclazole	13.8	189.2
4	Paclobutrazole	14.3	293.8
5	Hexaconazole	15.6	314.2
6	Diniconazole	17.8	326.2
7	Propiconazole	20.3	342.2
8	Tebuconazole	20.6	307.8
9	Epoxyconazole	21.7	329.8
10	Etoxazole	23.4	359.4
11	Fluquinconazole	24.6	376.2
12	Difenconazole	26.3	406.3

Figure 1 & Table 1 : Representative Chromatogram of twelve azole fungicides, retention times and molecular Mass

b) Optimization of Dispersive Liquid – Liquid Micro extraction

The effect of various experimental parameters were studied and optimized, including Selection of extraction solvent and dispersion solvent, extraction time and ionic strength. To evaluate the extraction efficiency under different conditions, extraction recovery and enrichment factor were used. The following equations 1 and 2 were used for calculation of enrichment factor (EF) and extraction recovery (R)

$$EF = \frac{C_{sed}/C_0}{C_0} \quad \text{----- 1}$$

$$R = \frac{C_{sed} \times V_{sed}}{C_0 \times V_0} \quad \text{----- 2}$$

Where,

C_{sed} = concentration of analyte in sedimented phase

C₀ = initial concentration of analyte in aqueous sample

V_{sed} = colume of sedimented phase

V₀ = volume of aqueous sample

c) Selection of Extraction Solvent

The extraction solvents were selected on the basis of higher density than water. The extraction capability of interested compounds immiscibility with water but miscibility in the dispersive solvent and good gas chromatography behavior. Based on this consideration C₆H₅Cl, CCl₄, C₂H₂Cl₄ and CHCl₃ were selected as potential extraction solvents. A series of sample solutions was test by using 0.7 mL of acetonitrile containing different volume of extraction solvent to achieve 10.0 μL volume of sediment phase. There by 16.0, 20.0 25.0 and 30.0 μL of C₆H₅Cl, CCl₄, C₂H₂Cl₄ and CHCl₃ were used respectively. C₂H₂Cl₄ had the highest extraction efficient in comparison to the other tested solvents. Consequently C₂H₂Cl₄ was selected as the optimal extraction solvent.

d) Selection of dispersive solvent

Miscibility of dispersive solvents in organic phase and aqueous phase is the critical for selection of dispersive solvent. Accordingly acetonitrile, acetone methanol and tetrahydrofuran were evaluated for this purpose. The enrichment factors using acetonitrile, acetone and tetrahydrofuran as dispersive solvents. According to the results acetonitrile was chosen as dispersive solvent.

e) Effect of extraction solvent volume

To examine the effect of extraction solvent volume, 0.7 mL of acetonitrile containing different volume of C₂H₂Cl₄ (15.0, 20.0 24.0 and 28.0 μL) was subjected to the same DLLME procedure. The extraction recoveries and enrichment factors verses volume of extraction solvent.

It was obvious that extraction recoveries for most of the analysts varied slightly, but enrichment factors decrease by increasing the volume of C₂H₂Cl₄. As a consequent 15.0 μL C₂H₂Cl₄ was selected to obtain high enrichment factor, good recovery and low detection limit.

f) Effect of dispersive Solvent volume

To obtain optimized volume of acetonitrile 0.4, 0.6, 0.9, 1.2 and 1.5 mL of acetonitrile containing the corresponding volume of C₂H₂Cl₄ were studied to attain the constant volume of the sedimented phase (6.0 ± 0.5 μL). The enrichment factors increased with the increase of volume of acetonitrile when it was less than 1.0 mL but decreased after the volume of acetonitrile exceeded 1.0 mL. Therefore, 1.2 mL was chosen as the optimum volume of the dispersive solvent.

g) Effect of Extraction Time

The effect of extraction time was examined in the range of 3-30 min with constant experimental conditions. It is revealed that after formation of a cloudy solution the surface area between extraction solvent and fruit sample phase was infinitely large, there by transition of analytes from fruit sample phase to extraction solvent was fast. Subsequently equilibrium state was estab-

lished rapidly so that the extraction time very short. In this 5 min as suitable for the procedure.

h) Effect of Salt Concentration (Ionic strength)

The salting-out effect is an important parameter in DLLME. Generally addition of salt decrease the solubility of target compounds in the aqueous sample and enhances their partitioning into the organic phase. For investigating the influence of ionic strength on extraction efficiency of DLLME, various experiments were performed by adding different amount of NaCl (0-10%w/v). The increase in ionic strength led to decrease in C₂H₂Cl₄ solubility in aqueous phase which increased the volume of sediment phase but decreased the enrichment factors. The enrichment factor decreases when the salt addition exceeded 1%, but extraction recoveries were almost constant. As a result a salt concentration of 1% was utilized.

i) Real Fruit Sample Analysis

Three Batches of Grape, Apple and Strawberry were collected from local super markets. The samples were pretreated as described in sample preparation extracted using DLLME procedure and analyzed by GC-MS. The results are summarized in Table 3.

It is revealed that the recommended method could be applied for the trace analysis of selected fungicides in real fruit samples.

IV. CONCLUSION

This work highlights an easy and quick simultaneous analytical method DLLME-GC-MS to quantify 12 azole fungicides in fruit samples (Tetraconazole, Penconazole, Tricyclazole, Propiconazole, Tebuconazole, Epoxyconazole, Etoazole, Fluquinconazole, Difenconazole).

The results of this study demonstrate that the proposed method provides the high enrichment factor and acceptable extraction recovery and repeatability. The proposed method was fits the requirement for the determination of selected fungicides in real fruit samples.

Table 2 : The recovery and relative standard deviations (n=5) for spiked fruit samples at two different concentration levels of fungicides from fruit samples

Fungicides	Spiked (μg/g)	Grape		Apple		Strawberry	
		RR (%)	(n=5) (%)	RR (%)	(n=5) (%)	RR (%)	(n=5) (%)
Tetraconazole	0.005	92.3	3.3	88.0	3.4	89.7	3.4
	0.05	88.3	4.0	89.3	3.4	91.3	3.3
Penconazole	0.005	88.3	4.6	88.3	4.0	85.3	4.1
	0.05	86.0	3.1	88.3	4.6	90.3	4.6
Tricyclazole	0.005	88.3	3.5	87.3	3.3	88.0	3.4
	0.05	89.0	3.4	88.0	3.4	88.0	4.5
Paclobutrazole	0.005	86.0	3.1	88.0	3.4	85.7	4.1
	0.05	91.7	3.3	92.7	3.5	88.7	4.0

Hexaconazole	0.005	88.0	3.0	92.7	3.5	89.3	2.8
	0.05	92.3	3.8	94.3	3.7	90.3	3.4
Diniconazole	0.005	85.3	3.6	84.7	3.0	85.3	3.6
	0.05	88.3	4.0	90.0	4.0	88.0	4.1
Propiconazole	0.005	88.3	4.0	91.7	3.3	91.0	4.0
	0.05	91.3	2.8	92.0	3.3	93.0	3.9
Tebuconazole	0.005	87.3	2.9	91.7	2.7	92.3	2.7
	0.05	91.3	3.8	92.7	3.5	94.3	2.7
Epoxyconazole	0.005	86.0	2.3	86.0	3.1	86.0	3.1
	0.05	89.0	3.0	91.7	3.8	93.3	4.5
Etoxazole	0.005	94.0	3.8	91.0	2.9	94.3	3.2
	0.05	95.0	3.2	94.3	2.7	95.0	3.2
Fluquinconazole	0.005	86.3	2.9	86.3	2.9	89.3	2.8
	0.05	88.7	4.0	93.7	3.7	92.3	2.7
Difenconazole	0.005	87.3	3.5	92.3	2.7	90.0	4.0
	0.05	95.0	2.8	92.7	3.5	90.7	4.2

RR = Relative Recovery

Table 3 : Concentrations of twelve fungicides in three batches of fruit samples

Fungicides Found ($\mu\text{g/g}$)	Grape (Batch)-($\mu\text{g/g}$)			Apple(Batch)-($\mu\text{g/g}$)			Strawberry(Batch)-($\mu\text{g/g}$)		
	1	2	3	1	2	3	1	2	3
Tetraconazole	ND	ND	ND	ND	ND	ND	0.05	ND	ND
Penconazole	ND	0.05	ND	ND	ND	ND	ND	ND	ND
Tricyclazole	ND	ND	ND	ND	ND	ND	ND	ND	ND
Paclobutrazole	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexaconazole	ND	0.02	ND	ND	ND	ND	ND	0.01	ND
Diniconazole	ND	ND	ND	ND	0.005	ND	ND	ND	ND
Propiconazole	0.01	ND	ND	ND	ND	ND	ND	ND	ND
Tebuconazole	ND	ND	0.02	ND	ND	ND	ND	ND	ND
Epoxy conazole	ND	ND	ND	ND	ND	ND	ND	ND	ND
Etoxazole	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fluquinconazole	ND	ND	ND	ND	ND	ND	ND	ND	ND
Difenconazole	ND	ND	0.01	ND	ND	ND	ND	0.005	ND

ND- Not Detected

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Effect of Cadmium Ion on Adsorption-Desorption Behavior of Simazine on Agricultural Soils

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Abstract - The effect of cadmium (Cd) on adsorption-desorption behavior of Simazine [2-chloro-4, 6 bis (ethylamine)-1,3,5-triazine] which is anionic herbicide were investigated at three different temperature 10, 25 and $40 \pm 1^\circ\text{C}$ on six agricultural soil samples which has different texture. The first order rate law was most fitted with the best correlation factor, the Linear, Freundlich and Langmuir models also were applied to describe the adsorption-desorption affinities to the soil samples. Values of adsorption rate constant k_a were in the range $0.836 - 1.818 \text{ h}^{-1}$ while desorption rate constant k_{des} were in the range $0.779 - 1.376 \text{ h}^{-1}$. The activation energy E_a^* for adsorption processes followed the range $11.041 - 17.684 \text{ KJmol}^{-1}$. Values of equilibrium constant $\ln K_o$ were in the range $0.048 - 0.278$. The standard free energy change ΔG° values were in the range -0.126 to $-0.655 \text{ KJmol}^{-1}$. Values of the standard enthalpy change ΔH° followed the range -2.702 to $-4.850 \text{ KJmol}^{-1}$. The value of standard entropy change ΔS° followed the range -7.557 to $-14.965 \text{ Jmol}^{-1}\text{k}^{-1}$. The negative values revealed that the adsorption-desorption processes spontaneously, exothermic and physical in nature to some extent and chemical in others.

Keywords : adsorption-desorption isotherms, simazine, thermodynamic parameter, UV-spectrophotometer.

GJSFR-B Classification : FOR Code: 961499, 300103



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Effect of Cadmium Ion on Adsorption-Desorption Behavior of Simazine on Agricultural Soils

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Abstract - The effect of cadmium (Cd) on adsorption-desorption behavior of Simazine [2-chloro-4, 6 bis (ethylamine)-1,3,5-triazine] which is anionic herbicide were investigated at three different temperature 10, 25 and 40 ± 1 °C on six agricultural soil samples which has different texture. The first order rate law was most fitted with the best correlation factor, the Linear, Freundlich and Langmuir models also were applied to describe the adsorption-desorption affinities to the soil samples. Values of adsorption rate constant k_a were in the range 0.836 - 1.818 h⁻¹ while desorption rate constant k_{des} were in the range 0.779 - 1.376 h⁻¹. The activation energy E_a^* for adsorption processes followed the range 11.041- 17.684 KJmol⁻¹. Values of equilibrium constant $\ln K_o$ were in the range 0.048 - 0.278. The standard free energy change ΔG° values were in the range -0.126 to -0.655 KJmol⁻¹. Values of the standard enthalpy change ΔH° followed the range -2.702 to -4.850 KJmol⁻¹. The value of standard entropy change ΔS° followed the range -7.557 to -14.965 Jmol⁻¹k⁻¹. The negative values revealed that the adsorption-desorption processes spontaneously, exothermic and physical in nature to some extent and chemical in others. The distribution coefficient K_d values for adsorption-desorption process varied between 2.369 - 2.611 mlg⁻¹, 5.556- 22.85 mlg⁻¹ respectively. Freundlich coefficient K_F ranged between 0.180-0.506 mlg⁻¹ for adsorption processes. The value Freundlich coefficient for desorption process K_{Fdes} ranged from 0.107 to 0.498 mlg⁻¹. Langmuir coefficient K_L for adsorption process varied between 0.027 - 0.064 mlg⁻¹. Langmuir coefficient K_{Ldes} values for desorption process from 0.014 to 0.067 mlg⁻¹. All desorption isotherms exhibited hysteresis.

Keywords : adsorption-desorption isotherms, simazine, thermodynamic parameter, UV-spectrophotometer.

I. INTRODUCTION

Estimating the behavior and fate of chemical pollutants in the environment is justified by the awareness that constitute serious risks for our health and other living organism⁽¹⁾. The sorption of an organic chemical on a soil is complicated process, which involves many sorbent properties, besides the physico-chemical properties of the chemical itself which are the relative amount of the mineral and organic material in soil and composition^(2&3). The different region of a soil matrix may contain different types, amounts, and distributions of surfaces of soil organic material⁽⁴⁾.

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The adsorption-desorption processes of a chemical on a solid from a water solution may be seen as the result of a reversible reaction which reaches a final equilibrium condition^(5&6). The sorption capacity of a given sorbent may depend on a series of properties, which are grain-size distribution, specific surface area, cation exchange capacity, pH, organic matter, and mineral constituents^(7&8). Hysteresis or nonsingularity in the adsorption-desorption processes, and its implications in the transport of these contaminants through soil^(9&10).

Temperature is another important factor that affected the adsorption-desorption processes, which may be occur through enthalpy-related force due to the electrostatic interactions. Or either through entropy-related force hydrophobic bonding due to London dispersion force⁽¹¹⁾. Simazine is anionic herbicide which belongs to triazine group^(12&13). Cadmium is typical pollutants it associates with various health problems. The adsorption-desorption behavior of the heavy metal coexists with the organic pollutants interaction with soil at different temperature (10, 25 and 40 ± 1°C) were investigated, the adsorption-desorption process pollutants in soil affects its transportation and bioavailability and hence is of great importance to environmental regulation and pollution control⁽¹⁴⁾.

II. MATERIALS AND METHODS

a) Soils

Fresh soil samples were taken from six soil samples were collected from six main agricultural, representing a range of physico-chemical properties. Subsamples of homogenized soils were analyzed for moisture content, organic matter content, particle size distribution, texture, pH, loss on ignition and exchangeable basic cations the detail were characterized in previous article⁽¹⁵⁾.

b) Pesticide

Analytical grad substituted Simazine (trade name Triamex), [2-chloro-4,6 bis (ethylamino)-1,3,5-triazine], (purity 98.8%), was purchased from Riedal-de Haen, Sigma-Aldrich company Ltd. Cd (NO₃)₂ used as analytical reagent for preparing working solution. All chemicals used were of analytical grade reagents and used without pre-treatments. Standard stock solutions of the pesticides were prepared in deionised water.

c) Adsorption-Desorption Experiments

The effect of cadmium on adsorption-desorption of Simazine from aqueous solution were determined at temperatures (10, 25, 40±1 C°) employing a standard batch equilibrium method^(11&16). Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (3, 5, 10, and 15 µg ml⁻¹) and (3, 5, 10, and 15 µg ml⁻¹) for Cd, at the soil solution ratios 2:10 in 16 ml glass tube fitted with Teflon-lined screw caps. The samples plus blanks (no pesticide) and control (no soil) were thermostated and placed in shaker for 0.5, 1, 3, 6, 9, 12 and 24h. The tubes were centrifuged for 20 min. at 3000 rpm. One ml of the clear supernatant was removed and analyzed for the pesticide concentration^(14&17). Simazine identification was done by spectrophotometer UV detector at wavelength 220 nm. Desorption processes were done as each test tube was placed in a thermostated shaker at (10,25,40 ±1 C°) after equilibration for 24 h with different pesticide concentrations (3, 5, 10 and 15 µg ml⁻¹) and (3, 5, 10, and 15 µg ml⁻¹) for Cd, the samples were centrifuged, 5ml of supernatant was removed from the adsorption equilibrium solution and immediately replaced by 5ml of water and this repeated for four times⁽¹⁸⁾. The resuspended samples were shaken for mentioned time previously for the kinetic study Simazine.

III. DATA ANALYSIS

a) Adsorption-Desorption Kinetics & Equilibrium constant

The rate constants for the effect of cadmium on adsorption-desorption of Simazine on soils were calculated using the first order rate expression^(19&20):

$$\log(C - C_t) = \log C - \frac{k}{2.303}t \quad (1)$$

Where k is k_a is the rate constant for adsorption (h⁻¹), t the time (h) C is C_o the concentration of pesticide added (µg ml⁻¹) and C_t the amount adsorbed (µg ml⁻¹) at time t. In all cases, first order equation provided satisfactory fit for the data as linear plots of log (C_o-C_t) against t for the effect of cadmium on adsorption-desorption of Simazine demonstrated in (Table 1). The same equation used to describe the process of desorption in all experiments and on all soil samples⁽²¹⁾. Where k is k_{des} is the desorption rate constant (h⁻¹), C_t is the amount of released pesticides at time t and C is C_e is the amount of released pesticides at equilibrium and k_{des} is the slope of straight line which is equal to coefficient release rate of k_{des}. A plot of log (C_e - C_t) versus t should give a straight line with slope -k_{des}/2.303 and intercept of log C_e for the effect of cadmium on adsorption-desorption of Simazine demonstrated in (Table 1).

Considering the experimental equilibrium constant k_o can be conducted by the ratio of adsorption rate constant k_a is to the desorption rate constant k_{des}, K_o were calculated using the following expression⁽²¹⁾.

$$K_o = \frac{k_a}{k_{des}} \quad (2)$$

i. Arrhenius activation energy

The Arrhenius activation energy E_a for the adsorption and desorption processes for the effect of cadmium on adsorption-desorption of Simazine on soils were calculated by linearized Arrhenius equation^(22&23):

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3)$$

Where k; adsorption rate constant or desorption rate constant, E_a; the activation energy, R; gas constant 8.314J (Kmol)⁻¹, and T; absolute temperature, A; preexponential factor, the plot of lnk against the reciprocal of absolute temperature resulted in straight lines for each system. The activation energies were evaluated from the slope of each linear plot as shown in table 2 for the effect of cadmium on adsorption-desorption of Simazine.

ii. Activations parameters

A plot of ln (k/T) against the reciprocal of absolute temperature for the effect of cadmium on adsorption-desorption of Simazine were shown in figure 1, the enthalpy of activation, ΔH*, and the entropy of activation, ΔS* were calculated from Eyring equation^(24&25):

$$\ln \frac{k}{T} = \ln \frac{k}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (4)$$

Where k; adsorption rate constant or desorption rate constant: ΔH*; enthalpy of activation, ΔS*; entropy of activation, k; Boltzmann's constant 1.38.10⁻²³ JK⁻¹, h; Plank's constants h=6.6.10⁻³⁴ Js. As shown in figure 3, the enthalpy of activation, ΔH*, and the entropy of activation, ΔS* were calculated from the slope and the intercept of each linear plot as shown in table2 for the effect of cadmium on adsorption-desorption of Simazine.

The free energies of activation, ΔG* for each system were determined by using the equations bellow⁽²⁶⁾.

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (5)$$

The values of ΔG* were determined at a T value which is equal to 298.15K, and these values are included in table 2 for the effect of cadmium on adsorption-desorption of Simazine.

iii. *Isosteric enthalpy of Adsorption*

The isosteric enthalpy of adsorption is the standard enthalpy of adsorption at a fixed surface coverage. Values of isosteric heat of the adsorption as a function of the amount of the chemical adsorbed (x) was calculated by the expression ⁽⁶⁾:

$$\Delta H = R \left[\frac{d \ln C_e}{d \left(\frac{1}{T} \right)} \right] x \quad (6)$$

Where C_e is the equilibrium concentration, and the average were calculated for each concentration, The results were summarized in table 2 for the effect of cadmium on adsorption-desorption of Simazine.

iv. *Standard free energy change*

Adsorptions equilibrium constant (K_o), can be expressed in terms of the standard Gibbs or free energy for adsorption (ΔG°) ⁽⁶⁾.

$$\Delta G^\circ = -RT \ln K_o \quad (7)$$

The results were summarized in table 3 for the effect of cadmium on adsorption-desorption of Simazine.

v. *Standard enthalpy and entropy change*

The standard enthalpy change of adsorption (ΔH°) represents the difference in binding energies between the solvent and the soil with the pesticides. Values of ΔH° and standard entropy change (ΔS°) also determined graphically from the following equation ^(6&10):

$$\ln K_o = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

Plotting $-\ln K_o$ against $1/T$, a straight line is expected the standard enthalpy change (ΔH°) of adsorption were determined from the slope, and the intercept equal to $\Delta S^\circ/R$ as shown in figure 2, the results were summarized in table 3.

b) *Adsorption-Desorption Isotherms*i. *Distribution Coefficient*

The distribution coefficient (K_d) was calculated by the using the following expression ^(6&19).

$$C_s = K_d C_e \quad (9)$$

The distribution coefficient (K_d) was calculated by taking the ratio of adsorption concentration in soil (C_s) and equilibrium concentration in solution (C_e), and averaged across all equilibrium concentration to obtain a single estimate of K_d for the effect of cadmium on adsorption-desorption of Simazine demonstrated in (Table 4 fig 3a). The same equations (9) used to describes the process of desorption in all experiments and on all soil samples the results was demonstrated in (Table 4 & fig 4a).

ii. *Freundlich Coefficient*

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation ⁽¹⁹⁾:

$$\log C_s = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

C_s and C_e were defined previously, K_F is Freundlich adsorption coefficients, and n is a linearity factor, it is also known as adsorption intensity, $1/n$ is the slope and $\log K_F$ is the intercept of the straight line resulting from the plot of $\log C_s$ versus $\log C_e$ as shown in (fig 3b). The values of K_F and $1/n$ calculated from this regression equation showed that Freundlich adsorption model effectively describes isotherms for Simazine in all cases. Desorption isotherms of pesticide was fitted to the linearized form of the Freundlich equation ⁽¹⁹⁾:

$$\log C_s = \log K_{Fdes} + \frac{1}{n_{des}} \log C_e \quad (11)$$

Where C_s is the amount of pesticides still adsorbed ($\mu\text{g g}^{-1}$), C_e is the equilibrium concentration of pesticides in solution after desorption ($\mu\text{g mL}^{-1}$), and K_{Fdes} ($\mu\text{g g}^{-1-n_{des}} / \text{ml}^{n_{des}} \text{g}^{-1}$) and n_{des} are two characteristic constants of Simazine desorption ⁽²³⁾. The value of the K_{Fdes} and n_{des} constants of Simazine demonstrated in (Table 4 & fig 4b).

iii. *Langmuir Adsorption Isotherm*

Data from the batch adsorption conform to Langmuir equation ⁽¹⁹⁾:

$$\frac{C_e}{C_s} = \frac{1}{C_m K_L} + \frac{C_e}{C_m} \quad (12)$$

C_m is the maximum amount of pesticide adsorbed (adsorption maxima, $\mu\text{g ml}^{-1}$), it reflects the adsorption strength and K_L is the Langmuir adsorption coefficient, binding energy coefficient. The results were summarized in (Table 4 & fig 3c).

The same equations (12) used to describes the process of desorption in all experiments and on all soil samples ⁽²⁰⁾ the results was demonstrated in (Table 4 & fig 4c).

c) *Hysteresis Coefficient*

A study for the effect of cadmium on adsorption-desorption of Simazine isotherms show positive hysteresis coefficients H_1 on the six selected soil samples. Hysteresis coefficients (H_1) can be determined by using the following equation ⁽²⁷⁾.

$$H_1 = \frac{n_a}{n_{des}} \quad (13)$$

Where n_a and n_{des} are Freundlich adsorption and desorption constants, respectively, indicating the greater or lesser irreversibility of adsorption in all samples, the highest values corresponding for which the highest adsorption constant was obtained. The coefficient H_1 is a simple one and easy to use, Data in table 5 demonstrated H_1 values for simazine.

The extent of hysteresis was quantified by using hysteresis coefficient (ω), it was defined on the discrepancy between the sorption and desorption isotherms, and calculated by using Freundlich parameters estimated from sorption and desorption isotherms separately, (ω) expressed as ⁽²⁰⁾:

$$\omega = \left(\frac{n_a}{n_{des}} - 1 \right) \times 100 \quad (14)$$

Zhu et. al ⁽²⁸⁾ proposed an alternative hysteresis coefficient (λ) based on the difference in the areas between adsorption and desorption isotherms, they derived the following expression for the parameter λ for the traditional isotherms:

$$\lambda = \left(\frac{n_a + 1}{n_{des} + 1} - 1 \right) \times 100 \quad (15)$$

IV. RESULTS AND DISCUSSION

Adsorption-desorption processes of simazine alone were discussed in our previous article ⁽¹³⁾, but in this study to investigate the effect of cadmium on adsorption-desorption behavior of Simazine depend on the interaction between the two that affected by the texture of the soil ⁽⁹⁾. The values of adsorption rate constant k_a were in the range 0.836-1.818 while, desorption rate constant k_{des} were in the range 0.779 - 1.376 for the effect of cadmium on adsorption-desorption of Simazine respectively as shown in Table 1. The nitrogen lone-pair electrons, side-chain NH group vise basic triazine ring N, and the Cl atom at the 2-position on the triazine rings all were available to formed complexes with Cd^{+2} ion and finally formation of adducts with organic matter of the soil ^(14&29). The Values of adsorption rate constant were greater than desorption constant indicating that adsorption processes was faster than desorption, and the values of adsorption-desorption rate constant decreased by increasing the temperature.

The activation energy E_a for adsorption processes followed the range 11.041-17.684 $KJmol^{-1}$, while for desorption processes followed the range 6.917-13.111 $KJmol^{-1}$ for the effect of cadmium on adsorption-desorption behavior of Simazine respectively. As the values of E_a for adsorption processes were higher than desorption. As shown from figures 1 a & b the values of R^2 in range 0.874 to 0.999

for adsorption process and 0.776 to 0.972 for desorption process, which supported our investigation that adsorption rate constant and amount adsorbed increased with the increase in organic matter content of soil, and an exothermic binding reaction and a reversible relation between temperature and the activation energy ^(20&26).

The Values enthalpy of activation, ΔH^* for adsorption-desorption followed the range-13.518 to-20.161 $KJmol^{-1}$, -12.247 to -15.589 $KJmol^{-1}$ for the effect of cadmium on adsorption-desorption behavior of Simazine respectively. The negative values of ΔH^* showing that the interaction of pesticides, heavy metal with the soil is an energetically stable exothermic process and the adsorption occurred through a bonding mechanism. As shown from figures the values of R^2 in range 0.821 to 0.980 which supported our investigation ⁽²⁵⁾. The values of isosteric enthalpy of adsorption were followed the range 959.04-1, 066.6 $KJmol^{-1}$, on selected soil samples. The values of isosteric heat of adsorption as a function of amount of chemical adsorbed, relatively small and were of the order which was consistent with a physical type of adsorption ⁽¹⁰⁾.

Data in table 2 demonstrated the values of entropy of activation ΔS^* followed the range-287.99 to -308.36 $Jmol^{-1} k^{-1}$, -275.33 to -296.39 $Jmol^{-1} k^{-1}$ for the effect of cadmium on adsorption-desorption behavior of Simazine respectively which suggest that the interaction done via the formation of ion-ion and hydrophobic interactions leading the decrease in the standard entropy ⁽²⁷⁾.

Data in table 2 demonstrated the values of free energy change ΔG^* values were in the range -96.79 to -109.95 $KJmol^{-1}$, and -88.99 to -101.1 $KJmol^{-1}$ for the effect of cadmium on adsorption-desorption behavior of Simazine respectively, indicating that the interactions were spontaneous with a high preference of the soil surface and adsorption occurred through a bonding mechanism⁽²⁸⁾.

Data in table 1 demonstrated the values of equilibrium constant K_o equilibrium constant for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine on selected soil samples were in the following from 1.049 to 1.321, while the values of equilibrium constant $\ln K_o$ were in the range 0.048 - 0.278, as shown in figure 2 confirming that K_o values were decreased with rise in temperature.

Data in table 3 demonstrated the free energy change ΔG^o values were in the range -0.126 to -0.655 $KJmol^{-1}$, all the values were negative and decreased with the rise in temperature, and thermodynamically spontaneous process and adsorption occurred through a bonding mechanism ^(29&30).

The values of enthalpy change ΔH^o followed the range -2.702 to -4.850 $KJmol^{-1}$, the results were summarized in table 3. The values of R^2 were in the

range 0.812 to 0.941 which supported the linear nature of the plot. The negative enthalpy indicating an exothermic binding reaction^(31&32), thus low values of ΔH° pointed toward chemisorptions, hence the heavy metal and the herbicides adsorption may be due to coordination and/or protonation, hydrogen bonding and dipole association or van der Waal's forces, and metal ion bridged mechanism between the clay and/or organic molecules occur with or without a water bridge. Our results showed that the negative values of ΔH° decrease with temperature. This indicates that the interactions between the pesticides and the studied soil samples were stronger at lower temperature.

The results were summarized in table 3 where the value of entropy change ΔS° followed the range -7.557 to -14.965 Jmol⁻¹ k⁻¹, a negative slope as shown in fig 2 $-\Delta H^\circ/T$ corresponds to positive change of entropy of the surroundings, and favors the adsorption. When temperature is raised $-\Delta H^\circ/T$ decreases and the increasing entropy of the surroundings which result, the equilibrium lies less to the adsorption process. The negative values of entropies pointing to the formation of the complexity by coordination or association of the herbicides and an exchangeable cation with the resultant of the loss in the degree of freedom of the pesticide^(33&34). The increase of the temperature from 288.15 to 308.15k leads to increase the thermal energy for the reactant and products combined with the decrease in the rate of adsorption reaction. On the other side, the increase in the thermal energy of the reactant and product leads to increase the disorder of reactant and product which decrease the bond energy formation for products of the reaction (adsorption).

Data in Table 4 demonstrates The distribution coefficient K_d values for adsorption process varied between 2.369 - 2.611 mlg⁻¹, and for desorption process varied between 5.556- 22.85 mlg⁻¹ for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine respectively, and the value of R^2 for adsorption-desorption process on selected soil samples ranged from 0.754 to 0.984 and from 0.752 to 0.968 respectively. The value of standard error (S.E.) for adsorption-desorption process ranged from 0.012 to 0.087 and from 0.016 to 0.087 respectively, our result agreed with article⁽³⁵⁾.

Coefficient K_F for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine ranged between 0.180-0.506 mlg⁻¹ and 0.107-0.489 mlg⁻¹ respectively. The value of n indicating a linear relationship as shown in figure 3 b & 4 b, the value of n ranged between 1.153-1.357, while Freundlich the value of n_{fdes} ranged between 1.071-1.807. The value of R^2 for adsorption-desorption process on selected soil samples ranged from 0.882 to 0.999 and from 0.764 to 0.998 respectively The value of standard error (S.E.) for adsorption-desorption processes ranged from 0.027 to 0.033 and from 0.026 to 0.043 respectively⁽³⁶⁾.

Langmuir coefficient K_L for adsorption process varied between 0.027 - 0.064 mlg⁻¹ while Langmuir coefficient K_{Ldes} values for desorption process varied between 0.014 - 0.067 mlg⁻¹. The values of C_m , S.E and R^2 demonstrated in table 4 for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine on selected soil sample. The, C_m , S.E, and R^2 ranged from, 8.929-18.18 μgg^{-1} , 0.030-0.037, and 0.760-0.935 for adsorption process respectively. While C_m , S.E, and R^2 ranged from 0.719-7.813 μgg^{-1} , 0.031-0.033, and 0.640-0.985 for desorption processes respectively⁽³⁷⁾.

Data in table 5 demonstrated (H_1) values for the effect of cadmium on adsorption-desorption behavior of Simazine from the selected soil samples in the range from 0.638-1.137, indicating an increase in the irreversibility of the adsorption of herbicide as the clay content increases, and indicate the increased difficulty of the sorbed analyte to desorb from the matrix. The calculated values of hysteresis coefficient (ω) for adsorption-desorption of for si for the effect of cadmium on adsorption-desorption of Simazine on the selected soil samples were summarized in table 5 ranged from 3 to 36. Whereas hysteresis coefficient (ω) is only applicable for the traditional type isotherms of the successive desorption⁽³⁸⁾. The data in table 5 demonstrated hysteresis coefficient (λ) for the effect of cadmium on adsorption-desorption of Simazine from the selected soil samples were ranged from 2 to 23.

V. CONCLUSION

The interaction of the heavy metal and organic pollutant bound to soil particles and its thermodynamic investigations important to pay more attention and more study to solve these problem. Adsorption-desorption experiments were conducted at 10, 25, and 40°C to study the parameter, which generally ascribed to H-bonding, van der Waals forces, electrostatic attraction, and coordination reactions with the active surfaces of the soil matrix, and also occur through the diffusion phenomena even through forming a bridge between the soil and the pollutant.

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Table 1 : Adsorption rate constants k_a , desorption rate constants k_d and equilibrium rate constants k_o for the effect of cadmium coexist with Simazine on the selected soil samples

Temp(K)	Parameter	Soils					
		S ₁	S ₂	S ₃	S ₄	S ₅	S ₆
283.15K	k_a (calc) h ⁻¹	1.565	1.818	1.636	1.631	1.513	1.730
	k_d (calc) h ⁻¹	1.284	1.376	1.284	1.324	1.289	1.340
	K_o	1.219	1.321	1.274	1.232	1.173	1.291
298.15K	k_a (calc) h ⁻¹	1.301	1.272	1.329	1.409	1.360	1.449
	k_d (calc) h ⁻¹	1.109	1.139	1.205	1.260	1.174	1.302
	K_o	1.173	1.117	1.104	1.119	1.158	1.158
313.15K	k_a (calc) h ⁻¹	0.842	0.909	1.042	0.956	0.892	0.836
	k_d (calc) h ⁻¹	0.794	0.836	0.966	0.884	0.849	0.779
	K_o	1.059	1.087	1.079	1.082	1.049	1.073

Table 2 : Thermodynamic parameters for the effect of cadmium on the adsorption-desorption Simazine at three temperatures and Isotheric heat change on the selected soil samples

Soil	E_a (kJmol ⁻¹), R ²		ΔH_a^* (kJmol ⁻¹), R ²		ΔS_a^* (Jmol ⁻¹ .K ⁻¹)		ΔG_a^* (KJmol ⁻¹)		average X(KJ/mol) Isotheric heat change
	Adsorpt ion	Desorp tion	Adsorpt ion	Desorp tion	Adsorpt ion	Desorp tion	Adsorpt ion	Desorp tion	
S ₁	-15.115 0.934	-11.714 0.938	-17.584 0.950	-14.184 0.956	-302.46	-292.24	-105.04	-98.68	970.64
S ₂	-17.027 0.999	-12.180 0.972	-19.496 0.999	-14.658 0.980	-308.36	-293.40	-108.66	-99.49	973.88
S ₃	-11.041 0.994	-6.917 0.890	-13.518 0.995	-9.387 0.935	-287.99	-275.33	-96.79	-88.99	959.04
S ₄	-12.995 0.920	-9.768 0.818	-15.464 0.941	-12.247 0.874	-294.65	-284.92	-100.66	-94.63	1,119.4

S ₅	-12.837 0.874	-10.134 0.890	-15.314 0.907	-12.612 0.924	-293.64	-286.58	-100.51	-95.48	1,025.8
S ₆	-17.684 0.902	-13.111 0.776	-20.161 0.922	-15.589 0.821	-301.53	-296.39	-109.95	-101.1	1,066.6

Table 3 : Equilibrium constants and standard free energy change at three different temperatures, Standard enthalpy change and standard entropy change (determined graphically) for the effect of cadmium on the adsorption-desorption Simazine on the selected soil samples

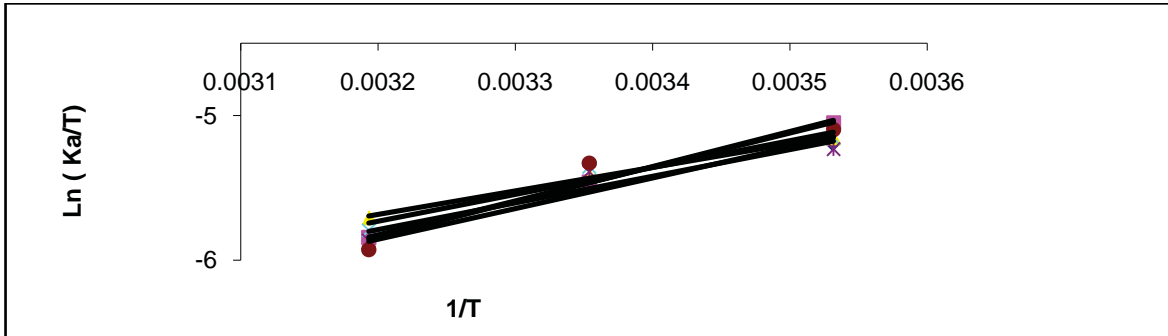
Soil	283.15 K		298.15K		313.15K		ΔH°_{cal} (KJ/mol)	R ²	ΔS°_{cal} J/(mol.k)
	lnK ₀	ΔG° (KJ/mol)	lnK ₀	ΔG° (KJ/mol)	lnK ₀	ΔG° (KJ/mol)			
S ₁	0.198	-0.465	0.159	-0.396	0.058	-0.152	-3.397	0.919	-10.259
S ₂	0.278	-0.655	0.111	-0.274	0.083	-0.217	-4.845	0.872	-14.965
S ₃	0.242	-0.570	0.099	-0.244	0.076	-0.197	-4.128	0.870	-12.712
S ₄	0.209	-0.491	0.112	-0.278	0.079	-0.204	-3.220	0.941	-9.711
S ₅	0.159	-0.376	0.147	-0.364	0.048	-0.126	-2.702	0.812	-8.089
S ₆	0.255	-0.601	0.107	-0.266	0.071	-0.184	-4.572	0.909	-7.557

Table 4 : Linear, Freundlich and Langmuir models for the effect of cadmium on the adsorption-desorption of Simazine at 298.15K on the selected soil samples

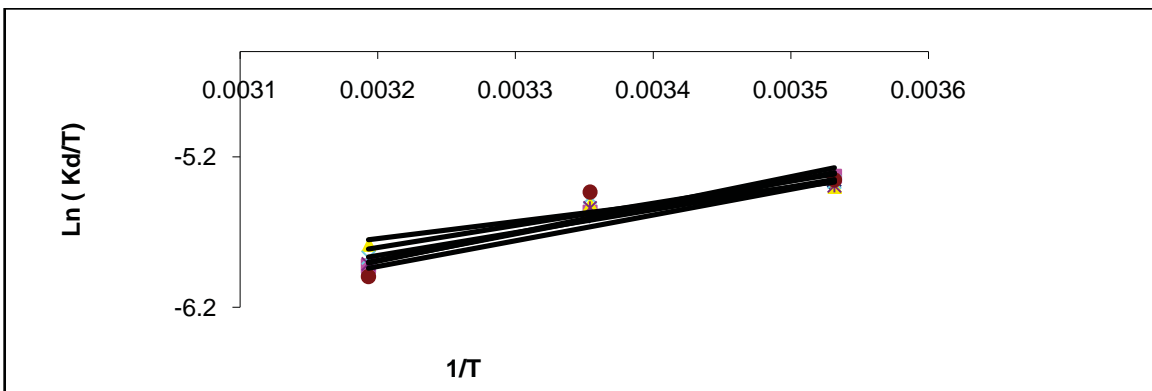
Models		Parameter	Soils						
			S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	
Adsorption	Distr	K _d (calc)	2.409	2.508	2.611	2.571	2.369	2.437	
		S.E	0.052	0.047	0.041	0.012	0.087	0.029	
		R ²	0.901	0.920	0.971	0.959	0.984	0.754	
	Freu	K _F (mL/g)	0.506	0.487	0.421	0.500	0.180	0.360	
		S.E	0.033	0.032	0.031	0.028	0.027	0.029	
		n _F	1.357	1.353	1.238	1.189	1.153	1.198	
	Lang	R ²	0.947	0.960	0.952	0.973	0.999	0.882	
		K _L (ml/g)	0.064	0.060	0.047	0.043	0.027	0.033	
		S.E	0.030	0.033	0.031	0.032	0.032	0.037	
	Desorption	Distr	C _m (μ g/g)	8.929	9.010	10.41	9.091	18.18	9.000
			R ²	0.761	0.935	0.760	0.845	0.870	0.765
			K _d (calc)	18.28	22.85	13.89	10.08	5.556	10.13
Freu		S.E	0.085	0.079	0.016	0.027	0.087	0.038	
		R ²	0.808	0.765	0.917	0.864	0.968	0.752	
		K _{Fdes} (mL/g)	0.432	0.449	0.107	0.261	0.498	0.209	
Lang		S.E	0.042	0.045	0.034	0.033	0.026	0.027	
		n _F	1.223	1.389	1.089	1.071	1.807	1.717	
		R ²	0.884	0.806	0.844	0.998	0.764	0.922	
Lang		K _L (ml/g)	0.056	0.067	0.028	0.014	0.015	0.053	
		S.E	0.078	0.011	0.063	0.034	0.035	0.050	
		C _m (μ g/g)	1.285	1.155	0.755	7.813	1.022	0.719	
R ²	0.643	0.640	0.932	0.748	0.960	0.985			

Table 5 : Hysteresis effect on desorption for cadmium coexist with Simazine on the selected soil samples

Soil	298.15K		
	H_1	ω	λ
S ₁	1.110	11	6
S ₂	0.974	3	2
S ₃	1.137	14	7
S ₄	1.110	11	6
S ₅	0.638	36	23
S ₆	0.698	30	19



a-



b-

Figure 1 : Variation of $\ln (K_a / T)$ with $1/T$ for the effect of cadmium coexist with Simazine of, (a) adsorption (b) desorption on the selected soil samples (\blacklozenge S₁, \blacksquare S₂, \blacktriangle S₃, \times S₄, $*$ S₅, \bullet S₆)

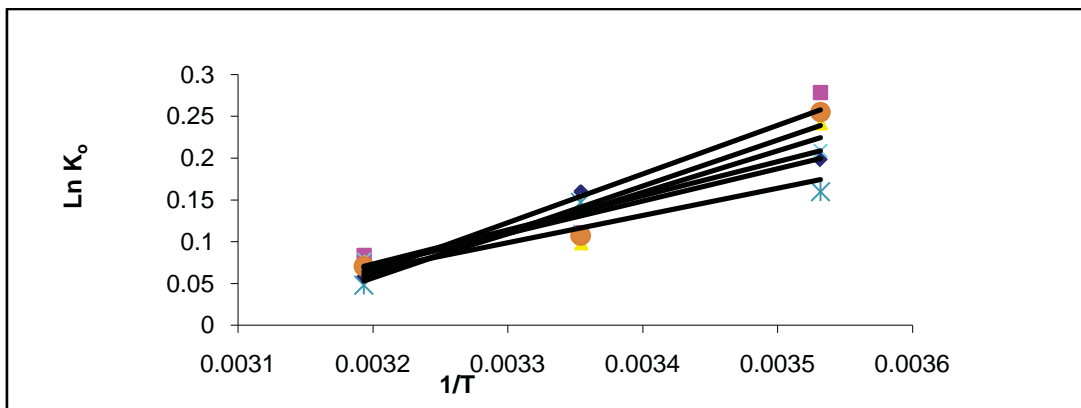
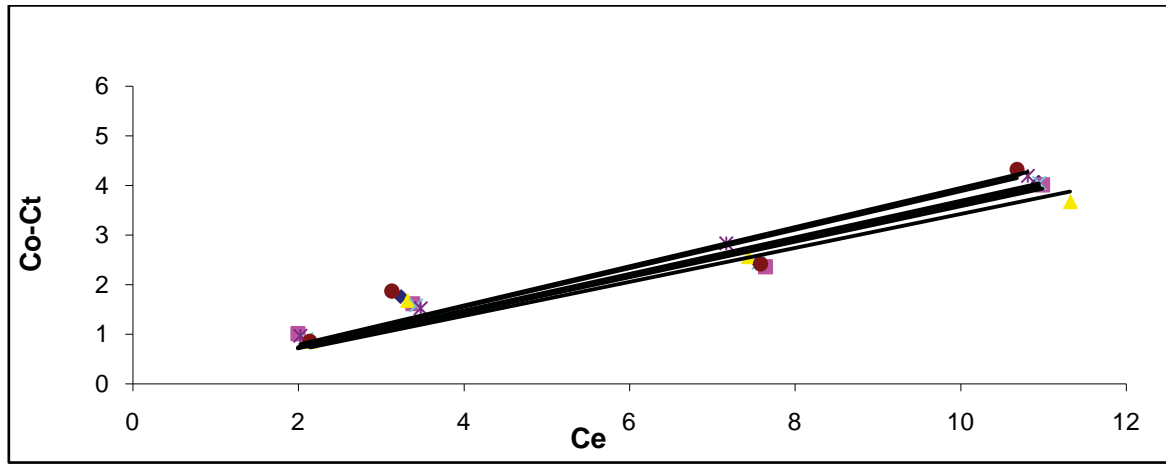
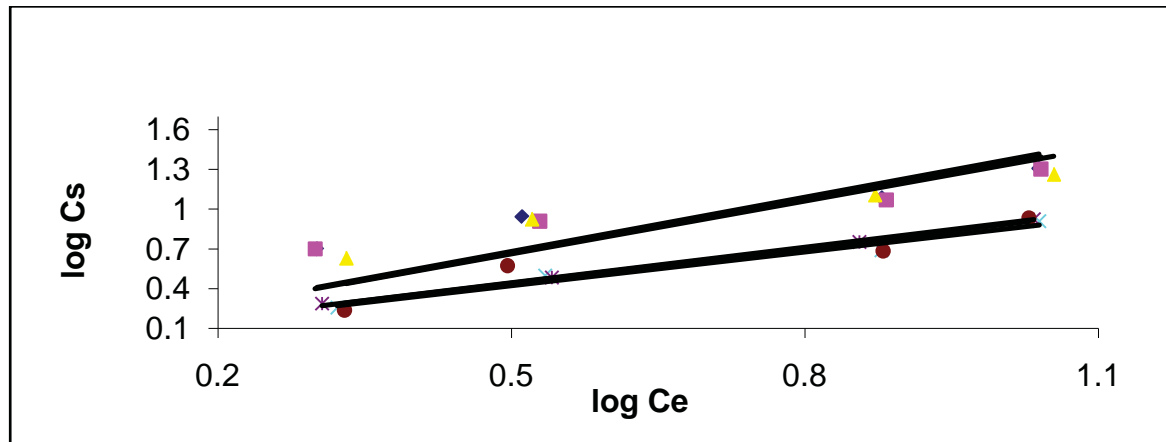


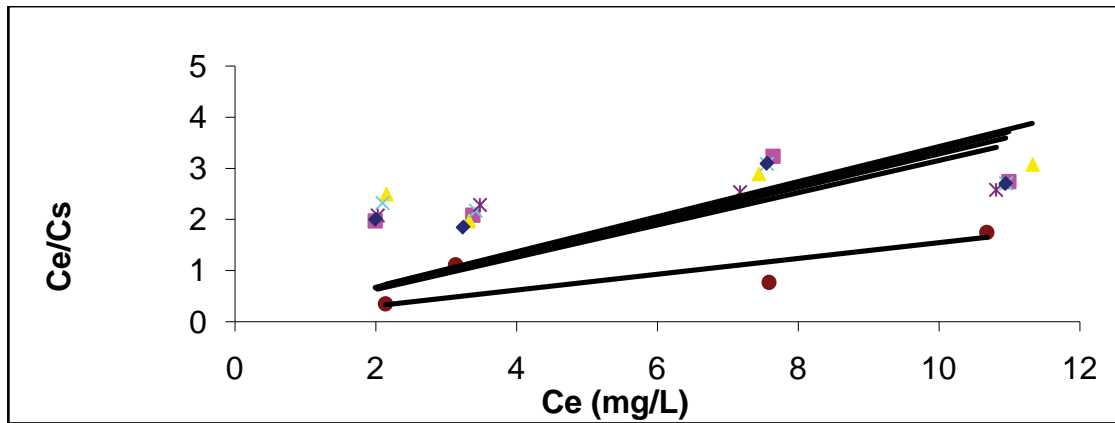
Figure 2 : Variation of $\ln K_0$ with $1/T$ for the effect of cadmium on the adsorption-desorption Simazine on the selected soil samples (\blacklozenge S₁, \blacksquare S₂, \blacktriangle S₃, \times S₄, $*$ S₅, \bullet S₆)



a-

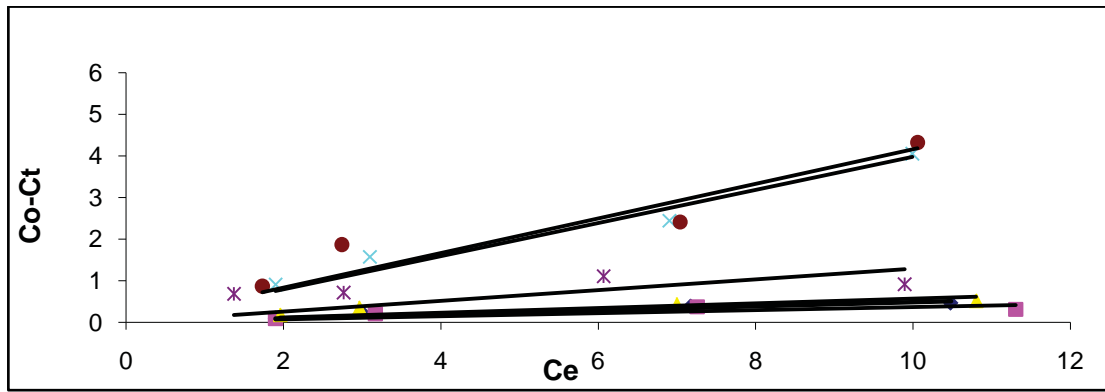


b-

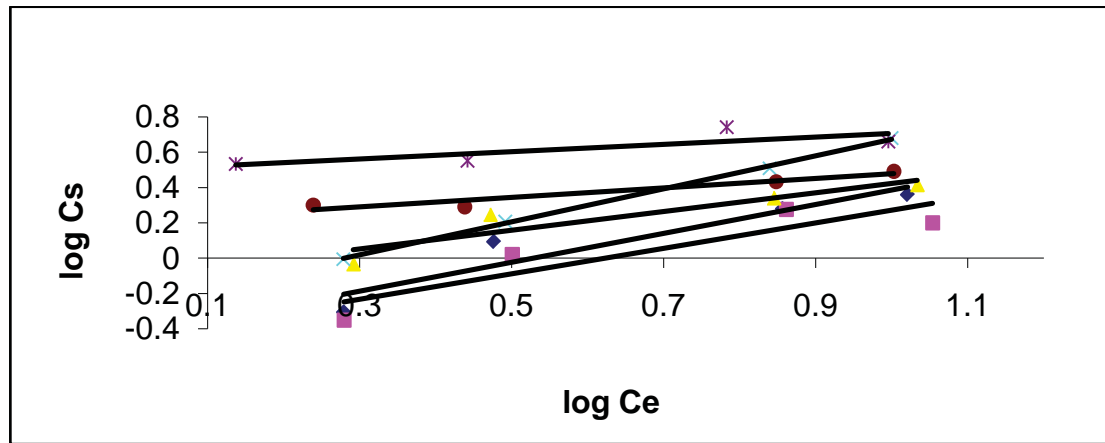


c-

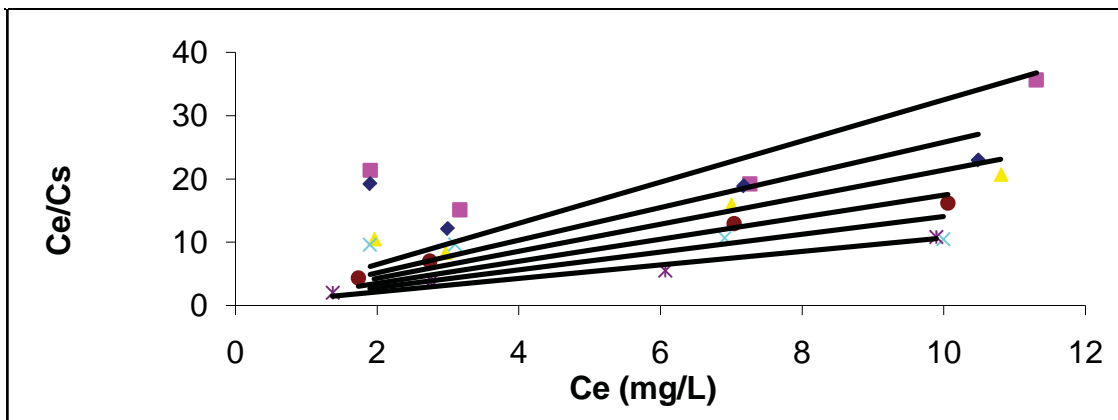
Figure 3 : Fitted models for the effect of cadmium on the Simazine adsorption (a) Linear (b) Ferundlich (c) Langmuir, on the selected soil samples (\diamond S₁, \blacksquare S₂, \blacktriangle S₃, \times S₄, $*$ S₅, \bullet S₆)



a-



b-



c-

Figure 4 : Fitted models for the effect of cadmium on the Simazine desorption (a) Linear (b) Ferundlich (c) Langmuir, on the selected soil samples (\diamond S₁, \blacksquare S₂, \blacktriangle S₃, \times S₄, $*$ S₅, \bullet S₆)

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Results:

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently. You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.



Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.
- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

Discussion:

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.



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<i>References</i>	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring



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