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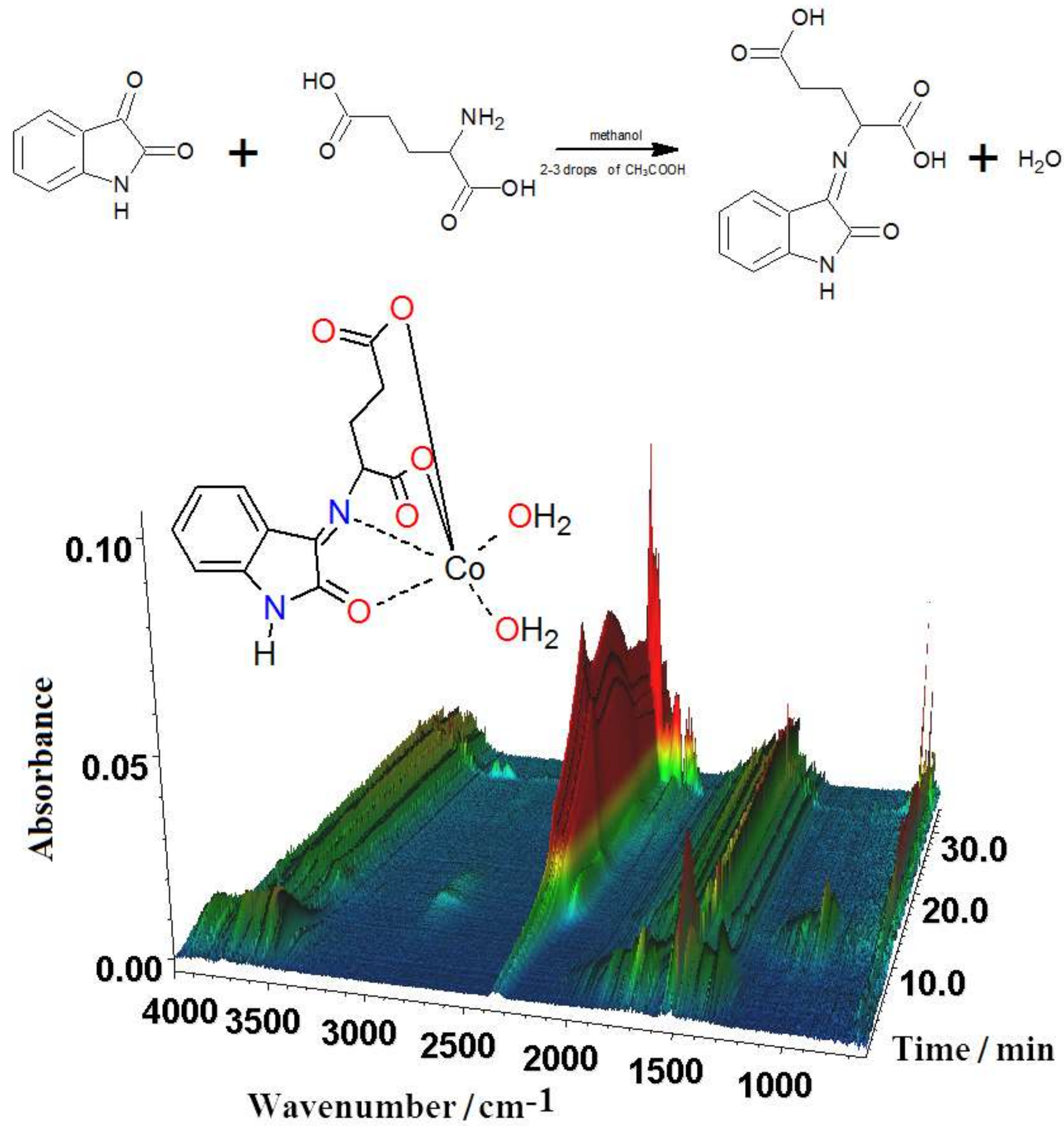

Complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand formed by condensation reaction of isatin with glutamic acid

Hydrodeoxygenation and pyrolysis of free fatty acids obtained from waste rendering fat

Determination of paracetamol in pharmaceutical samples by spectrophotometric method

Major and minor head losses in a hydraulic flow circuit: experimental measurements and a Moody's diagram application

A comprehensive review of database resources in chemistry

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Editorial

Wishing that all people may pass well in this worrying period of covid-19, the Editor is pleased to announce the third issue of this year containing interesting topics for the readers. This issue is opened with the description of monoclinic or triclinic forms of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes successfully synthesized with a ligand resulting from the condensation reaction of isatin and glutamic acid. Physico-chemical properties of complexes were extensively investigated by elemental analysis, XRF, XRD, FTIR, TG–DSC and TG–FTIR methods and magnetic measurements. It is well known that non-edible fats are a common renewable feedstock for the biofuels production to avoid partially the use of edible feeds and fossil fuels. Thus, the use of waste rendering fat to produce pyrolyzed and hydrogenated oils was described. The feedstock was hydrolyzed producing free fatty acids and glycerol plus residues. The free fatty acids were pyrolyzed with and without metal sulfides metal supported catalyst or hydrotreated separately. In the sequence, a spectrophotometric method is described to determine paracetamol concentration in 7 pharmaceutical formulations, using 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine as coupling agent. This easy procedure is based on the reaction of paracetamol acid hydrolysis to p-aminophenol that reacts with nitrite to form diazonium ion, which is coupled with coupling agent to produce azo dyes easily analyzable. Lately, it has been observed that the cities' rapid expansion led the domestic and industrial hydraulic drainage networks to become gradually more complicated. Dealing with this subject, the following paper contributes to the evaluation of the major and minor head losses in a hydraulic flow circuit and compares the simulated results with the Moody's diagram application, having observed an extremely low absolute deviation. This issue is closed with an interesting article in education in chemistry section on how to distinguish between databases that are efficient and objective for literature searches and revises important points of the database for chemists. It concludes that substance and citation data bases that covers almost all areas of chemistry, have become an invaluable tool in bibliometric analysis.

The Editor and his team wish to express their sincere thanks to authors for their great contributions, and reviewers for their outstanding manuscripts evaluation.

Assis Vicente Benedetti
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[2] Wendlant, W. W., Thermal Analysis, Wiley-Interscience, New York, 3rd ed., 1986, ch1.

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SUMMARY

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Original article
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Complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand formed by condensation reaction of isatin with glutamic acid

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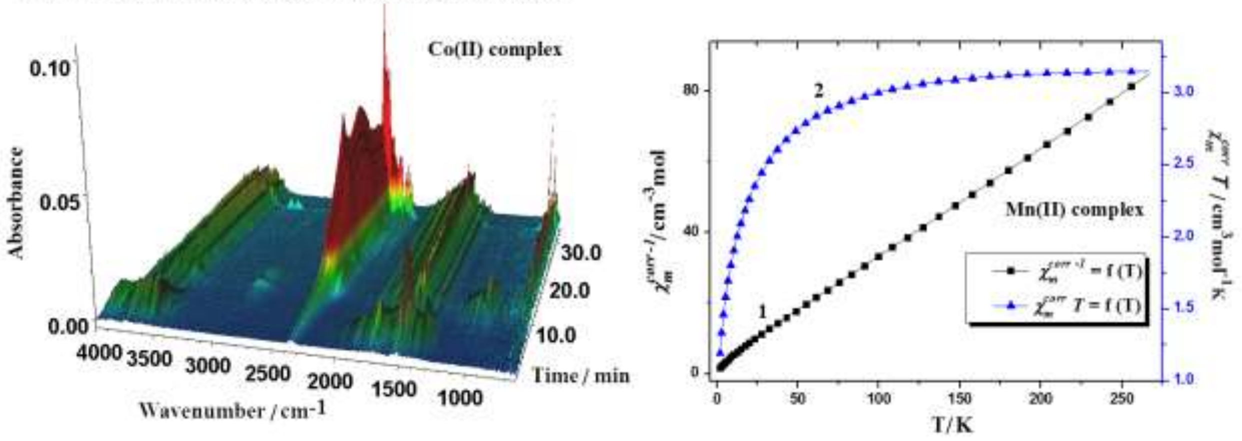
ABSTRACT: The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand ($H_2L=C_{13}H_{12}N_2O_5$) formed by condensation reaction of isatin and glutamic acid were synthesized. Their physico-chemical properties were characterized using elemental analysis, XRF, XRD, FTIR, TG–DSC and TG–FTIR methods and magnetic measurements (Gouy's and SQUID-VSM methods). The complexes were obtained in crystalline forms (monoclinic or triclinic) with the formulae: $M(LH)_2{\cdot}nH_2O$ for Mn(II), Ni(II) and Zn(II) and $ML{\cdot}nH_2O$ for Co(II) and Cu(II), where $LH=C_{13}H_{11}N_2O_5^{-}$, $L^{-}=C_{13}H_{10}N_2O_5^{2-}$, n = 1 for Mn(II), Cu(II) and Zn(II), n = 2 for Co(II) and n = 3 for Ni(II). In air at 293–1173 K they decompose in three steps forming finally the oxides of the appropriate metals. The gaseous decomposition products were identified as: H_2O, CO_2, CO, hydrocarbons and N_2O. The magnetic moment values for complexes (except Zn(II) complex) show their paramagnetic properties with the ferro- and antiferromagnetic interactions between central ions. The compounds of Mn(II) and Co(II) are high spin complexes with weak ligand field. In Co(II) and Cu(II) complexes two carboxylate groups take part in the metal ion coordination while in those of Mn(II), Ni(II) and Zn(II) only one carboxylate anion coordinates to central ion.

The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand (H_2L, $L=C_{13}H_{10}N_2O_5^{2-}$) formed by condensation reaction of isatin and glutamic acid were synthesized and their physico–chemical properties studied.



1. Introduction

A type of ligand such as isatin (1H-indole-2,3-dione) creates an interesting basis of current research in inorganic and coordination chemistry due to its wide applications and diverse biological properties. It plays an important role such as: antibacterial, antifungal, anticonvulsant, anti-HIV and antiviral[1-7]. From literature survey, it appears that isatin heterocycles exhibit manifold

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importance in the field of medicinal chemistry. It is used for the design and development of anticancer drugs[1,2]. There are over ten thousand biologically active compounds containing indole core. More of them are approved as commercially available drugs or are undergoing clinical trials. Antioxidant potential of the thiosemicarbazone derivatives was analysed by *in vitro* free radical scavenging assay[8]. Therefore, derivatives of isatin based on the thiosemicarbazone are potential compounds with wide range of promising biological properties which may be explored further for the treatment of several diseases. Likewise, isatin structural scaffold could act as DNA inhibitors. The isatin compound hybrids have the potential to overcome the drug resistance[9].

Isatin and its derivatives are one of the most important and broadly occurring structural units in several natural compounds. As a natural substance it occurs in plants while as metabolite in the human body[10-16].

Isatin is sparingly soluble in ether. From water, alcohol and acetic acid it crystallizes in red needles form that melt at 200 – 201ºC[17]. Its structure may cause the electrophilic substitution or nucleophilic addition on the carbonyl group carbon atom.

The metal complexes of isatin were found to have pharmacological properties and some of them, especially Co(II) compounds, can form the interesting group of single–molecule magnets (SMMs) with special magnetic applications[18-22]. They show magnetization hysteresis at low temperature occurring the special property of macroscopic magnets and possess a finite magnetization that can be frozen in the absence of an applied magnetic field. At low temperatures, these systems can be considered as a magnet since the relaxation of the magnetization becomes significantly slow[22].

Isatin metal compounds with amino acids are little known. Only a few information about the synthesis of isatin and amino acid ligands are available in the literature[23,24]. Therefore, their studies are important for understanding the relationship between chemical structure and biological macrocycle activities that may indicate their practical use as models in biochemistry systems. Thus, the chemistry of metal complexes with multidentate ligands as isatin with amino acids can gain much interest. The toxicity towards various bacteria, the cytotoxic and inhibitory effects of the obtained compounds on some cells and examination of their impact on living organisms seem interesting.

The aim of our investigations was to synthesize the complexes of new ligand synthesized in reaction of condensation of isatin and glutamic acid, 2-(2-oxoindolin-3-ylideneamino)pentanedioic acid ($C_{13}H_{12}N_2O_5$) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions and to characterize them by various physico-chemical measurements.

2. Experimental

2.1. Materials

All chemicals and solvents used for the syntheses were of commercially available reagent grade and applied without further purification.

2.1.1. Synthesis

Ligand (Scheme 1) was synthesized by refluxing glutamic acid (0.01 mol L^{-1}) (1.47 g) with isatin (0.01 mol L^{-1}) (1.47 g) in 100 mL methanol aqueous solution (99% pure, Aldrich Chemical Company). For the reaching of equilibrium state the solids in solutions were constant heating for 2–3 h in the presence of three drops of glacial acetic acid. They were filtered off, washed with water and methanol and dried at 303 K to constant masses.

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) with ligand were prepared by adding the equivalent quantities of methanol solutions of metal chlorides (3.6 mmol): $MnCl_2{\cdot}4H_2O$ (710 mg), $CoCl_2{\cdot}6H_2O$ (860 mg), $NiCl_2{\cdot}6H_2O$ (860 mg), $CuCl_2{\cdot}2H_2O$ (610 mg) and $ZnCl_2$ (490 mg) (analytically pure, Polish Chemical Reagents in Gliwice – Poland) to a warm methanol solution of H_2L (3.6 mmol, 1000 mg) in the round bottom flask. The pH of solution was adjusted by water ammonia solution dropwise to pH value about 6.5 – 7. Then the reaction mixture was refluxed for 6 – 8 h. It was cooling at room temperature and after partial evaporation filtered off, washed with water and methanol and dried at 303 K to constant mass.

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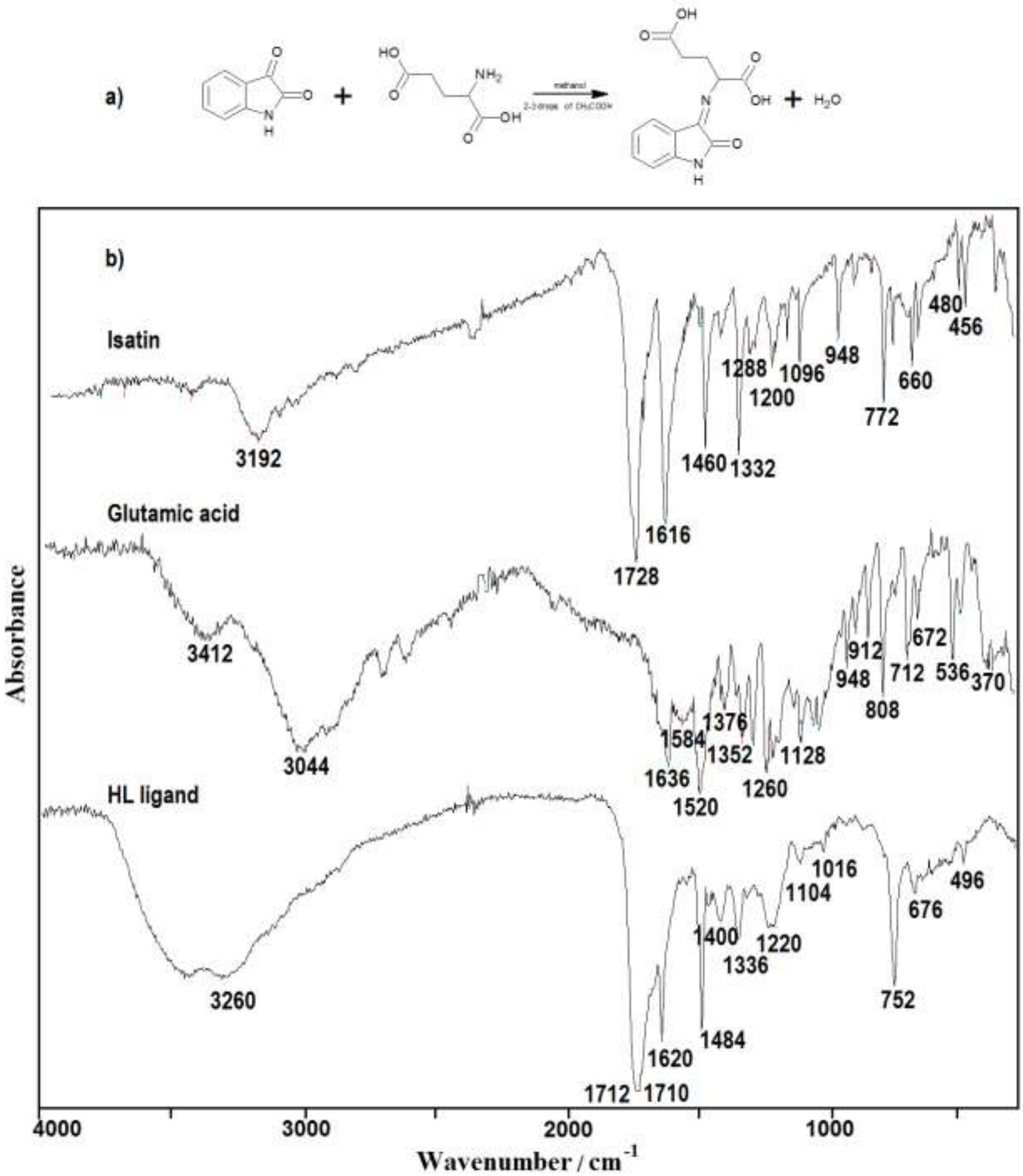


Scheme 1. a) Ligand synthesis, b) FTIR spectra of components used for the synthesis.

2.2. Methods and apparatus applied

The contents of carbon, hydrogen and nitrogen were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyser. The amounts of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metals were established by X-ray fluorescence XRF method with the use of spectrophotometer of X-ray fluorescence with energy dispersion EDXRF-1510 (Canberra-Packard).

The FTIR spectra of complexes and the products of the intermediate and final complex decompositions were recorded over the range of 4000 – 400 cm^{-1} using an M-80 Perking-Elmer spectrometer. The samples were prepared as KBr discs.

The ^{1}H-NMR spectrum for ligand and Zn(II) compound in DMSO-d_6 was recorded on a Bruker Avance 300 MHz NMR spectrometer at 298.1 K.

The X-ray diffraction patterns of compounds and of their residues after final decomposition processes were taken on a HZG-4 (Carl-Zeiss. Jena) diffractometer with Ni filtered CuK$_\alpha$ radiation. The measurements were made within the range of $2\theta = 4^o – 80^o$ by means of Bragg-Brentano method.

The thermal stability and decomposition of the complexes were studied in air using a Setsys 16/18 (Setaram) TG, DTG and DSC instrument. The experiments were carried out under air flow rate of 20 mL min^{-1} in the range of 297 – 1173 K at a heating rate of 5 K min^{-1}. The initial masses of samples used for measurements changed from 7.85 to 4.09 mg and were heated in Al_2O_3 crucibles.

The TG–FTIR measurements of Mn(II), Co(II) and Zn(II) complexes were performed to identify their gaseous decomposition products on the Q5000 TA apparatus coupled with the Nicolet 6700 spectrophotometer. The experiments were carried out under a dynamic nitrogen atmosphere in flowing nitrogen of 20 mL min$^{–1}$ in open platinum crucibles. The complexes were heated up to 1273 K at a heating rate of 20 K min$^{–1}$. The gaseous decomposition products were analysed over the range of 4000 – 400 cm^{-1} using the Nicolet 6700 spectrophotometer.

Magnetic susceptibility of polycrystalline samples of transition metal compounds was investigated at 76 – 303 K and for some of them at 2 – 300 K. The measurements in the range of 76 – 303 K were carried out using the Gouy's method. Mass changes were obtained from Cahn RM-2 electrobalance. The calibrate employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be $1.644 \cdot 10^{-5}$ cm^3 g^{-1}. The measurements were made at a magnetic field strength of 9.9 kθe. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants[25].

The effective magnetic moment values were calculated from the Eq. 1:

$$\mu_{eff} = 2.83\ (\chi_m \cdot T)^{1/2} \qquad (1)$$

where: μ_{eff} - effective magnetic moment, χ_m – magnetic susceptibility per molecule and T - absolute temperature.

The measurements in the range of 2 – 300 K were carried out with the use of Quantum Design SQUID – VSM magnetometer at magnetic field 0.1 T. The superconducting agent may generally operate at a field strength ranging from 0 to 7 T. The SQUID magnetometer was calibrated with the palladium rod sample.

3. Results and Discussion

All synthesized compounds were obtained as powders with the different colours changing from brownish pink, via brown to brick-red ones. Elemental analysis, XRF and thermogravimetric experimental data confirmed them to be hydrated. The molar conductance, magnetic and infrared spectroscopy measurements were made to estimate their structure. The compounds were obtained with general formulae $M(LH)_2 \cdot nH_2O$ for Mn(II), Ni(II) and Zn(II) and $ML \cdot nH_2O$ for Co(II) and Cu(II), where $LH = C_{13}H_{11}N_2O_5^–$, $L = C_{13}H_{10}N_2O_5^{2–}$, n = 1 for Mn(II), Cu(II) and Zn(II), n = 2 for Co(II) and n = 3 for Ni(II). Some predictions about the compositions of compounds may be compatible with those in literature[26-30]. In the cited papers the ways of Cu(II) and Pd(II) ion coordination with ligand formed by the glutamic acid and various organic compound condensation reactions are presented. Not having identical compositions to those used by us, these arrangements show that one deprotonated glutamic carboxylic acid group may coordinate to metal ions. As we did not determine the complex structures this fact let us also state the formulae of compounds, especially for Cu(II) and Co(II) ones.

The results of elemental and XRF analyses are as follows:

Ligand $C_{13}H_{12}N_2O_5$, Yield: 78.98% as a brown solid. Anal. Calc. for ligand (%): C, 56.52; H, 4.38; N, 10.14. Found: C, 57.42; H, 4.60; N, 9.85.

$Mn(LH)_2 \cdot H_2O$, Yield: 75.63% as a light brown solid. Anal. Calc. for $MnL_2 \cdot H_2O$ (%): C, 50.09; H, 3.89; N, 8.99; Mn, 8.81. Found: C, 50.82; H, 4.08; N, 8.83; Mn, 7.87. IR: 3384 (ν_{OH}), 3216 ($\nu_{N–H}$), 1724 ($\nu_{C=O})_{ket.}$, 1712 (ν_{COOH}), 1690 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 (ν_{HC-N}), 1408 (δ_{C-H}), 1296 ($\nu_{sCOO–}$), 1196 (ν_{C-N}), 1104 (ν_{Ar}), 752 (δ_{CH}), 580 ($\nu_{M–O}$) cm^{-1}, 416 ($\nu_{M–N}$) cm^{-1}.

$CoL \cdot 2H_2O$, Yield: 83% as a brownish pink solid. Anal. Calc. for $CoL \cdot 2H_2O$ (%): C, 42.41; H, 3.57; N, 7.61; Co, 16.01. Found: C, 41.82; H, 4.06; N, 7.07; Co, 16.19. IR: 3340 (ν_{OH}), 3230 ($\nu_{N–H}$), 1725 ($\nu_{C=O})_{ket.}$, 1692 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468

($\nu_{HC\text{-}N}$), 1400 ($\delta_{C\text{-}H}$), 1336 ($\nu_{sCOO–}$), 1196 ($\nu_{C\text{-}N}$), 1104 (ν_{Ar}), 752 (δ_{CH}), 644 ($\nu_{M–O}$) cm^{-1}, 460 ($\nu_{M–N}$) cm^{-1}.

Ni(LH)$_2$·3H$_2$O, Yield: 73.11% as a brown solid. Anal. Calc. for NiL$_2$·3H$_2$O (%): C, 47.07; H, 4.26; N, 8.45; Ni, 8.88. Found: C, 47.30; H, 4.26; N, 7.96; Ni, 9.20. IR: 3376 (ν_{OH}), 3200 ($\nu_{N–H}$), 1704 ($\nu_{C=O})_{ket.}$, 1692 (ν_{COOH}),1680 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 ($\nu_{HC\text{-}N}$), 1404 ($\delta_{C\text{-}H}$), 1328 ($\nu_{sCOO–}$), 1196 ($\nu_{C\text{-}N}$), 1104 (ν_{Ar}), 752 (δ_{CH}), 580 ($\nu_{M–O}$) cm^{-1}, 456 ($\nu_{M–N}$) cm^{-1}.

CuL·H$_2$O, Yield: 84.87% as a brown solid. Anal. Calc. for CuL·H$_2$O (%): C, 43.89; H, 3.41; N, 7.87; Cu, 17.86. Found: C, 42.96; H, 3.80; N, 7.28; Cu, 17.50. IR: 3440 (ν_{OH}), 3340 ($\nu_{N–H}$), 1724 ($\nu_{C=O})_{ket.}$, 1696 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 ($\nu_{HC\text{-}N}$), 1408 ($\delta_{C\text{-}H}$), 1328 ($\nu_{sCOO–}$), 1216 ($\nu_{C\text{-}N}$), 1104 (ν_{Ar}), 756 (δ_{CH}), 680 ($\nu_{M–O}$) cm^{-1}, 488 ($\nu_{M–N}$) cm^{-1}.

Zn(LH)$_2$·H$_2$O, Yield: 60.50% as a brick-red solid. Anal. Calc. for ZnL$_2$·H$_2$O (%): C, 49.27; H, 3.82; N, 8.84; Zn, 10.32. Found: C, 49.43; H, 4.12; N, 9.35; Zn, 10.03. IR: 3332 (ν_{OH}), 3248 ($\nu_{N–H}$), 1724 ($\nu_{C=O})_{ket.}$, 1688 (ν_{COOH}), 1680 (ν_{asCOO^-}), 1620 ($\nu_{C=N}$), 1468 ($\nu_{HC\text{-}N}$), 1396 ($\delta_{C\text{-}H}$), 1340 ($\nu_{sCOO–}$), 1220 ($\nu_{C\text{-}N}$), 1088 (ν_{Ar}), 748 (δ_{CH}), 640 ($\nu_{M–O}$) cm^{-1}, 460 ($\nu_{M–N}$) cm^{-1}.

The complexes are insoluble in most of the organic solvents except methanol and acetonitrile.

The ^{1}H-NMR spectrum for H$_2$L was recorded in DMSO-d$_6$. The experimental results were not suitable for fair interpretation due to their poor quality, high ratio of background noise to signals and d-electron nature so the results were not presented in this article.

In order to estimate the electrolytic properties of these compounds dissolved in methanol their molar conductance were measured and they were found to be in the range of 8.23 – 33.67 S cm^2 mol^{-1} indicating the analysed complex solutions not to be electrolytes since their molar conductance worths are less than 70 S cm^2 mol^{-1} [23,24].

3.1. Thermal analysis

The thermal stability of complexes was studied in air at 293 – 1173 K (Tab. 1, Fig. 1). When heated to 1173 K they decompose in three stages. First they dehydrate in one step and next being gradually decomposed form ultimately the oxides of appropriate metals with the intermediate formations of oxycarbonates, M$_2$OCO$_3$ or their mixtures with the metal oxides.

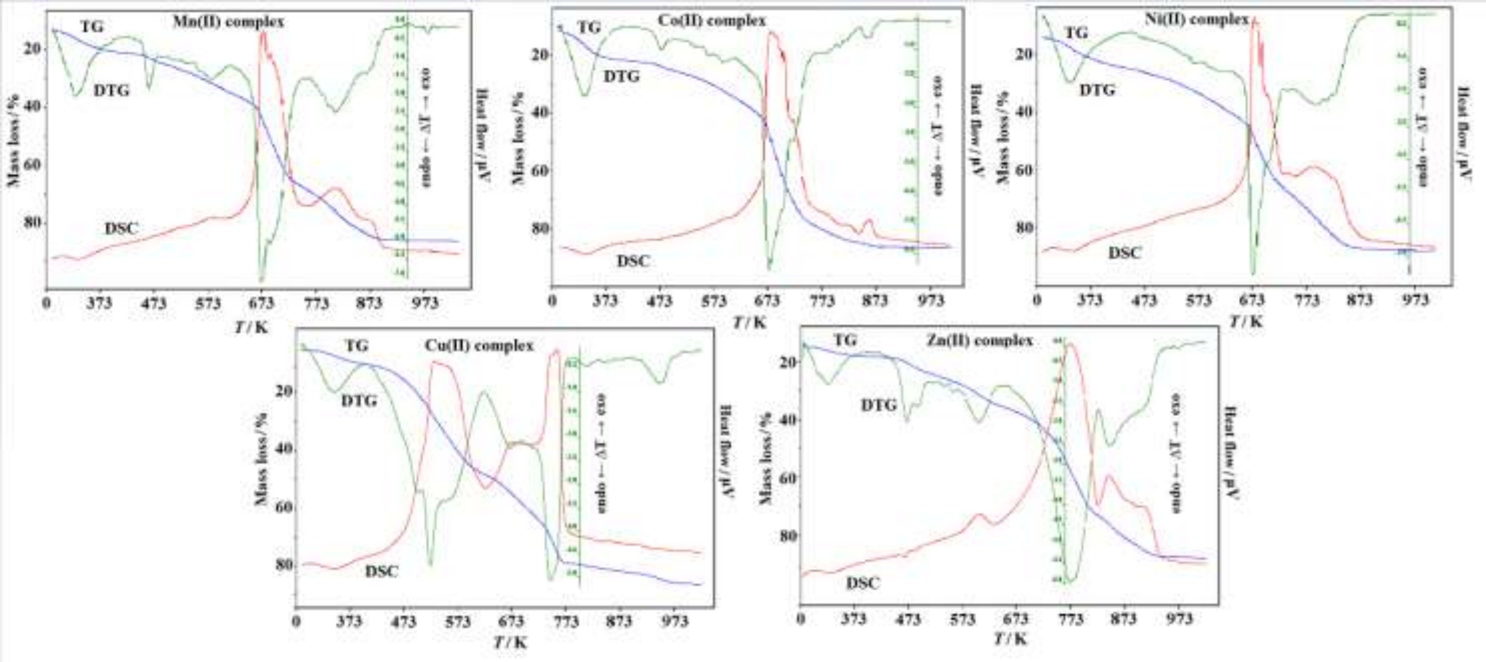


Figure 1. TG, DTG and DSC curves for analysed complexes.

Table 1. Temperature ranges of thermal stability for analysed complexes in air at 293 – 1173 K, their dehydration process and enthalpy values.

Complex	ΔT_1 / K	Mass loss / %		n°	ΔT_2 / K	Mass loss / %		Residue mass / %		T_K/ K	ΔH /	ΔH^o /
		calc.	found			calc.	found	calc.	found		kJ mol^{-1}	kJ mol^{-1}
$Mn(LH)_2 \cdot H_2O$	310-394	10.40	10.09	4	419-900	86.37	86.36	13.63	13.64	906	52.88	13.22
$CoL \cdot 2H_2O$	310-390	11.70	12.00	2	423-873	88.85	88.27	11.15	11.73	893	51.40	25.70
$Ni(LH)_2 \cdot 3H_2O$	323-414	12.82	12.45	3	436-970	88.98	89.90	11.01	10.10	973	30.93	10.31
$CuL \cdot H_2O$	323-404	5.07	5.02	1	413-1013	85.47	85.02	14.53	14.98	1023	37.78	37.78
$Zn(LH)_2 \cdot H_2O$	323-388	4.45	4.46	1	423-903	87.44	88.25	12.56	11.75	923	17.74	17.74

$HL^-=C_{13}H_{11}N_2O_5^-$, $L=C_{13}H_{10}N_2O_5^{2-}$, ΔT_1 - temperature range of dehydration process, n – number of water molecules lost in one step, ΔT_2 - temperature range of anhydrous complex decomposition, T_K – final temperature of decomposition process, ΔH^o - enthalpy value for one molecule of water.

The complexes are stable up to 310–323 K. In the range of 310 – 414 K they dehydrate with an endothermic effect losing all water molecules. The found enthalpy values for one water molecule of dehydration process change from 10.31 to 37.78 kJ mol^{-1}. On further heating of compounds at 413 – 1013 K the oxycarbonates, M_2OCO_3 of the corresponding metals were formed[31] but in the case of Ni(II) and Zn(II) complexes the mixtures of Ni_2OCO_3 and Zn_2OCO_3 with NiO and ZnO were identified. The final products of complex decompositions were following oxides: MnO_2, CoO, NiO, CuO and ZnO. They were identified by X-ray analysis data. For example Fig. 2 presents the diffractogram of the final product of Ni(II) compound decomposition.

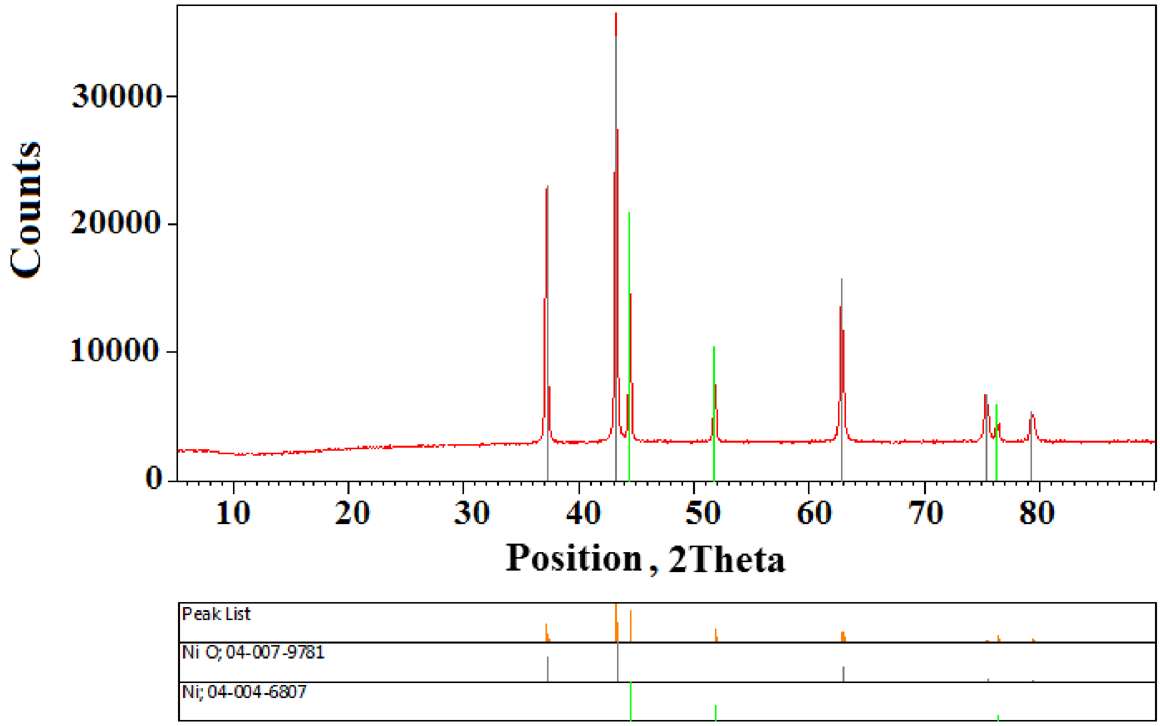


Figure 2. The X-ray powder diffractogram of the final product of decomposition for Ni(II) compound.

The residue masses calculated from TG curves are equal to 10.10–14.98%, while those theoretical were 11.01–14.53%.

The coordination number values of central ion depend mainly on the kind of cation[32,33]. In order to determine them it is necessary to estimate the positions of water molecules in analysed compounds. Not having monocrystal structure data of compounds we can only estimate them taking into account their initial dehydration process temperature values. If water molecules are lost in one step below 423 K they may form outer sphere water[32]. However, if they are coordinated weakly with central atom, they may be released also at low temperature indicating this way their outer sphere character. Then in the presented complexes it is difficult to state if water molecules are in outer or inner coordination positions.

3.2. TG–FTIR Analysis

The TG–FTIR coupled technique was applied for analysed complexes of Mn(II), Co(II) and Ni(II) to identify their gaseous decomposition products. For example the FTIR spectra of the volatile components of mixture evolved during destruction of Co(II) complex are presented in Figs. 3 and 4. Their interpretations reveal that H_2O, CO_2, CO and hydrocarbons are released during heating to 1173 K[34,35]. The heating of Co(II) complex leads to the release of water molecules up to about 393 K. The FTIR spectra show characteristic bands in the regions: 4000–3600 and 1700–1400 cm^{-1} (Fig. 3) due to stretching and deformation vibrations of water molecules[34]. Next, the intensity of gases evolved during heating increases. It is connected with the great liberation of CO_2 molecules. The FTIR spectra show bands at 3800 – 3500 cm^{-1}, 2400 – 2300 cm^{-1} and at about 900 cm^{-1} coming from stretching and deformation vibrations of carbon dioxide. The maximum amounts of CO_2 are observed after 20 minutes of heating at about 580 K. The FTIR spectra show as well the characteristic bands derived from N_2O at 1250 – 1100 cm^{-1} and ammonia molecules at about 1000 – 800 cm^{-1}. Additionally, the bands at 1200 and

1000 cm^{-1} derived from the rocking vibrations of C–H resulting from the $(CH_3)_2N$ moiety are observed[34,35]. Another volatile products of Co(II) compound thermal decomposition in nitrogen are hydrocarbons. Therefore FTIR spectrum contains the bands at 3300 – 3100 cm^{-1}, 1700 – 1650 cm^{-1} and 1500 – 1400 cm^{-1} coming from their molecule stretching vibrations[34,35]. Above 700 K the bands at 2200 – 2100 and 800 cm^{-1} resulting from carbon monoxide vibrations occur. Their highest intensities appear after 30 minutes of heating[34].

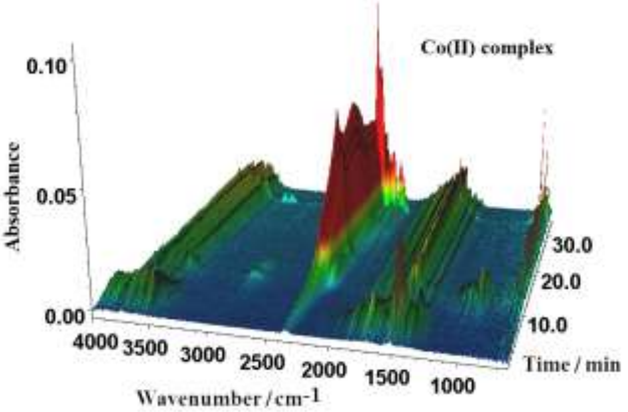


Figure 3. The FTIR spectrum of gaseous products evolved during the decomposition of Co(II) compound.

3.3. X-Ray powder diffraction

X–Ray powder diffraction of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes indicated them to be a crystalline compounds. A number of crystallization trials to obtain the single crystals of analysed complexes with several different solvents (such as H_2O, alcohols, DMSO, DMF and acetonitrile) have been carried out. The compounds were dissolved in pure solvent as well as in solvent mixture. Crystallization test were performed both at room temperature and at 8 °C.

Due to the lack of monocrystals of analysed compounds suitable for measurements, estimation of the unit cell parameters was carried out applying the Dicvol06 programme[36,37] (Tab. 2) using the X–ray powder diffraction data. According to the obtained results all analysed complexes were found to form low symmetry compounds. The complexes of Mn(II), Co(II), Cu(II) and Zn(II) crystallized in monoclinic system while that of Ni(II) in triclinic one[36,37]. All experimental data (angular values and lattice constants of primitive cell) are showed in Tab. 2. The X-ray diffraction patterns and dependences of I/I_0 *vs.* 2θ of analysed complexes are presented in Figs. 5 and 6.

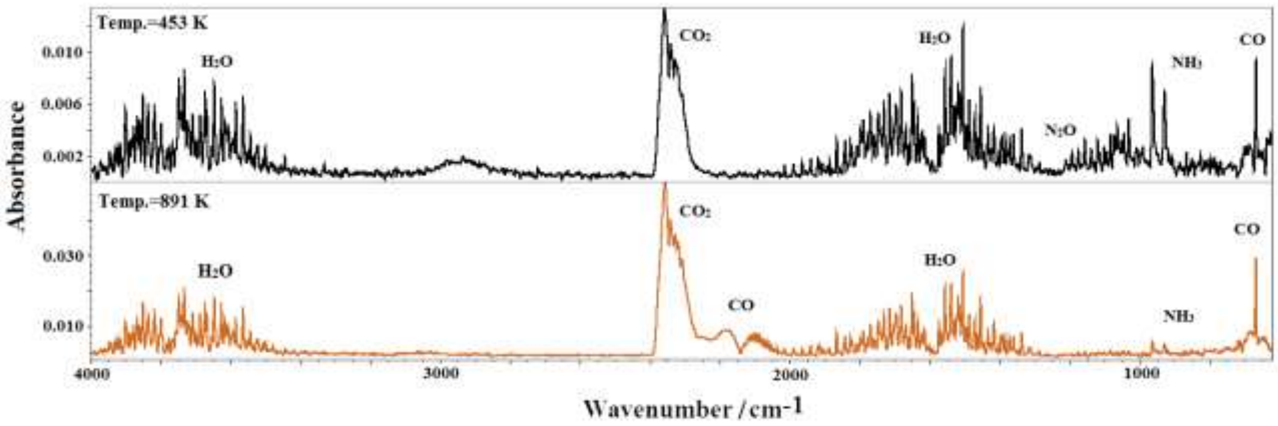
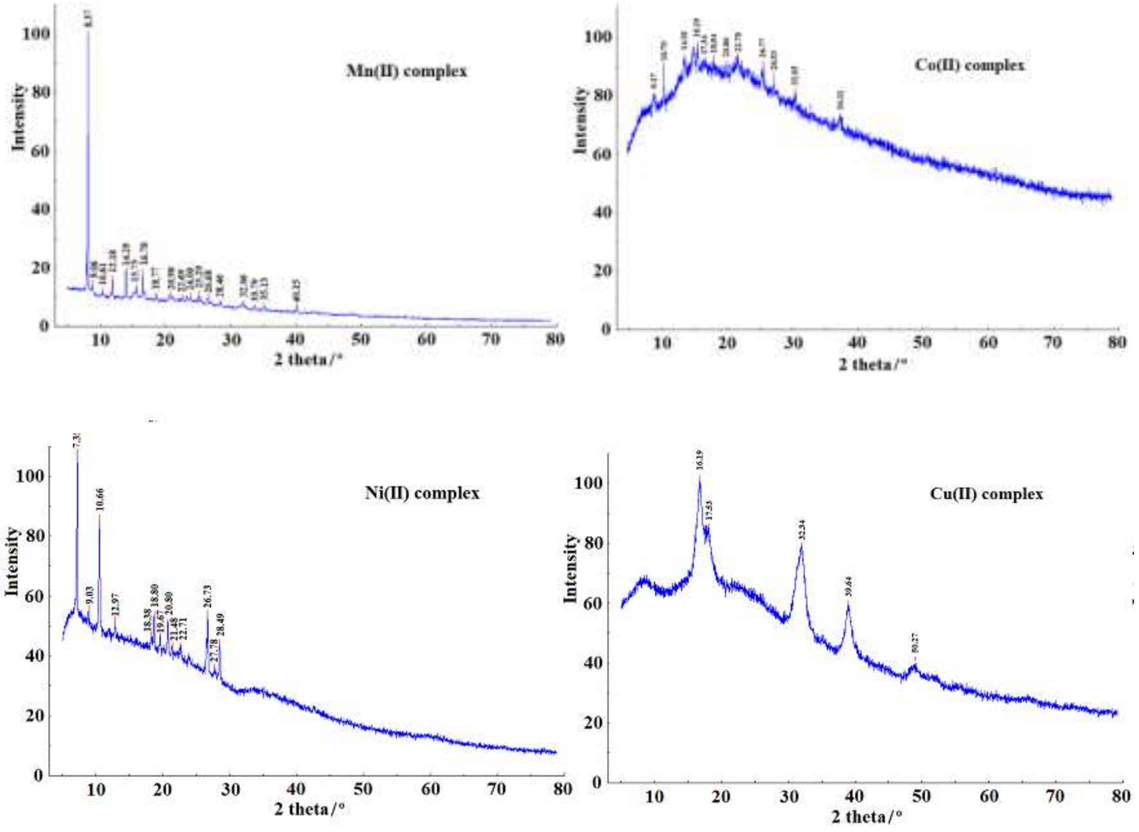


Figure 4. The FTIR spectra of gaseous products for Co(II) complex decomposition in N_2 at 453 and 891 K.

Table 2. The data of unit cell parameters (*α, β, γ, a, b, c* and *V*) obtained for analysed complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the use of Dicvol 06 programme, HL=$C_{13}H_{11}N_2O_5^{-}$, L=$C_{13}H_{10}N_2O_5^{2-}$.

	$Mn(LH)_2 \cdot H_2O$	$CoL \cdot 2H_2O$	$Ni(LH)_2 \cdot 3H_2O$	$CuL \cdot H_2O$	$Zn(LH)_2 \cdot H_2O$
a / Å	17.19	8.47	8.26	7.16	12.31
b / Å	5.77	9.57	11.98	12.37	7.66
c / Å	25.27	15.79	15.15	8.85	13.79
α / °	90.00	90.00	94.54	90.00	90.00
β / °	94.77	95.65	91.16	91.12	96.40
γ / °	90.00	90.00	90.19	90.00	90.00
V / Å^3	2499.42	1273.57	1494.81	793.53	1292.42



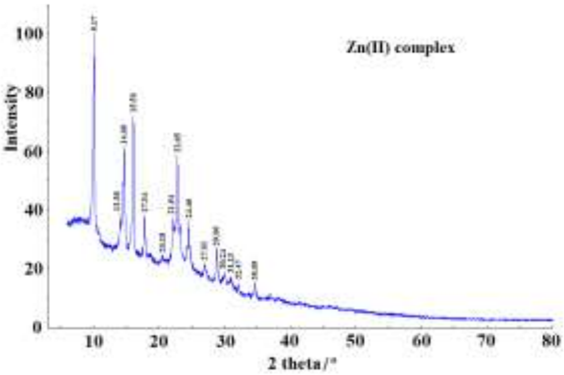


Figure 5. X-ray diffractograms for analysed complexes.

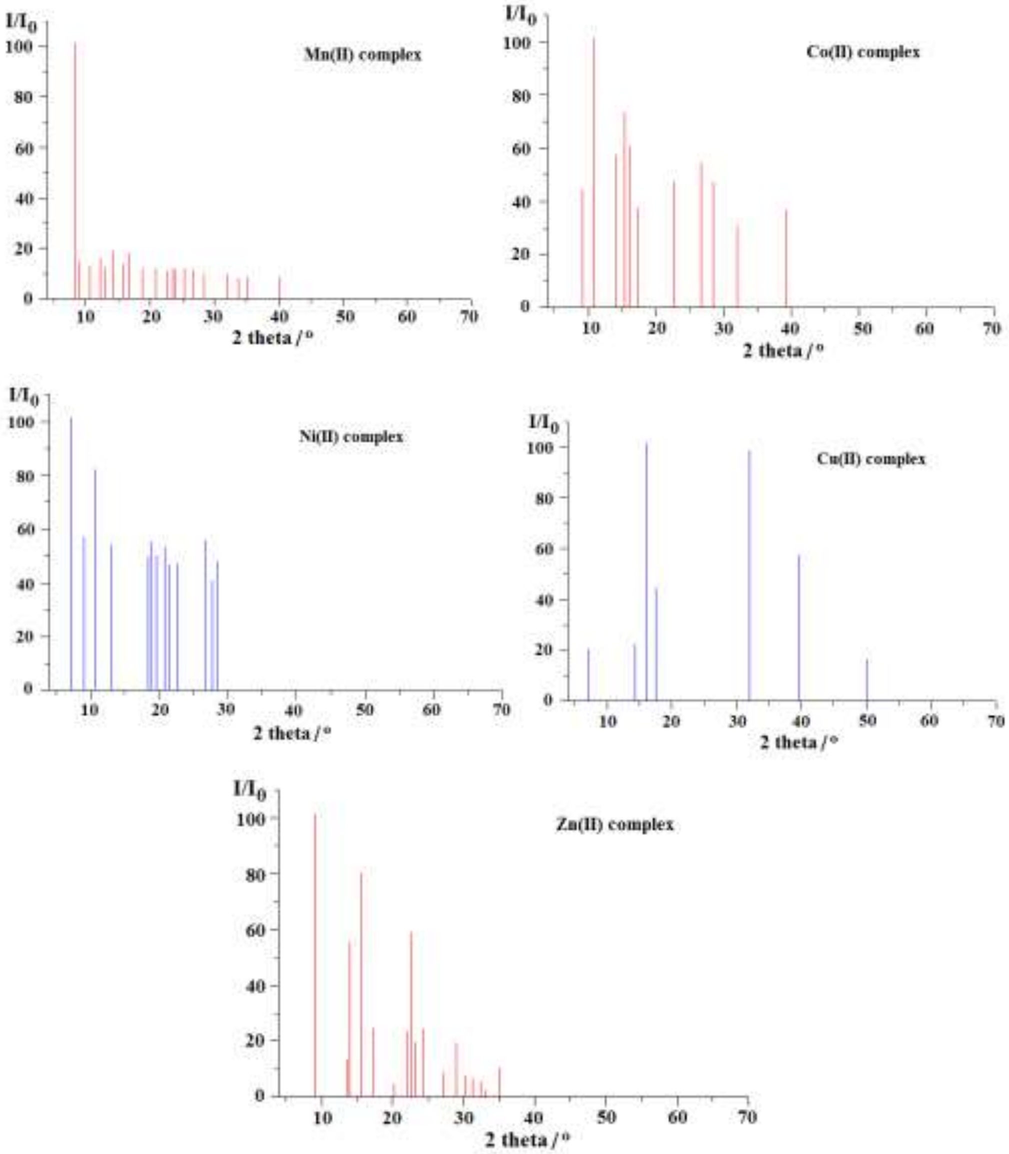


Figure 6. Dependence of I/I_0 vs. 2θ for Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) compounds.

3.4. Infrared spectra

The IR spectrum of ligand exhibits a broad band at 3260 cm^{-1} assigned to the N–H stretching vibration mode, ν(H–N)[34,35]. Also in its spectrum the strong sharp ketonic band of indole group vibration, ν(C=O), appears at 1710 cm^{-1}. A clear band of stretching vibration due to C=N, ν(C=N), appears at 1620 cm^{-1} and band at 1484 cm^{-1} comes from stretching vibration of HC–N group, ν(HC–N). The stretching vibration of C=O from COOH group yields the band at 1712 cm^{-1}, ν(C=O). In the spectrum of ligand, the bands of C=C stretching vibrations, ν(C=C), and C–H scissoring vibrations, δ(C–H), are at 1104 and 752 cm^{-1}, respectively.

In the spectra of analysed complexes, the new wide bands at 3440 – 3332 cm^{-1} appear indicating the presence of water molecules in compounds. It is in good agreement with the results of the elemental analysis and thermogravimetric data. The stretching vibration bands of N–H group, ν(N–H), are present in the region of 3340 – 3200 cm^{-1}. The ketonic bands of indole C=O group vibrations, ν(C=O), occur in their spectra from 1725 to 1704 cm^{-1}. A strong band due to C=N stretching vibrations, ν(C=N), appears at 1620 cm^{-1}. In complex spectra the HC–N vibration band is present at 1468 cm^{-1}. In the spectra of Co(II) and Cu(II) complexes there is not characteristic band of carboxylic acid stretching vibration ν_{COOH} at 1712 cm^{-1} that is splitted into two band peaks of asymmetric and symmetric carboxylate stretching vibrations, ν_{asCOO-} *and* ν_{sCOO}, at 1692 and 1696 cm^{-1} and 1336 and 1328 cm^{-1}, respectively, (Tab. 3). It indicates that two carboxylate anions take part in the metal ion coordination.

Table 3. The frequencies of maximum, cm^{-1}, of absorption bands in FTIR spectra of ligand and its compounds with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), HL=$C_{13}H_{11}N_2O_5^-$, L=$C_{13}H_{10}N_2O_5^{2-}$.

Ligand	$Mn(LH)_2 \cdot H_2O$	$CoL \cdot 2H_2O$	$Ni(LH)_2 \cdot 3H_2O$	$CuL \cdot H_2O$	$Zn(LH)_2 \cdot H_2O$	
–	3384	3340	3376	3440	3332	ν_{OH}
3260	3216	3230	3200	3340	3248	ν_{N-H}
1712	1712	–	1692	–	1688	ν_{COOH}
1710	1724	1725	1704	1724	1724	$\nu_{C=O\ ket}$
–	1690	1692	1680	1696	1680	ν_{asCOO-}
1620	1620	1620	1620	1620	1620	$\nu_{C=N}$
1484	1468	1468	1468	1468	1468	$\nu_{HC–N}$
1400	1408	1400	1404	1408	1396	$\delta_{C–H}$
–	1296	1336	1328	1328	1340	ν_{sCOO-}
1220	1196	1196	1196	1216	1220	ν_{C-N}
1104	1104	1104	1104	1104	1088	ν_{Ar}
752	752	752	752	756	748	$\delta_{C–H}$
–	580	644	580	680	640	ν_{M-O}
–	416	460	456	488	460	ν_{M-N}

Bands of CH in plane scissoring vibration, δC–H, bands of C-Car asymmetric ring vibration, νAr, bands of O-H stretching vibration, νOH, bands of C=O stretching vibration, νC=O.

In the case of Mn(II), Ni(II) and Zn(II) complex spectra there are bands of carboxylic acid stretching vibrations, ν_{COOH}, at 1712, 1692 and 1688 cm^{-1} resulting from one carboxylic group that does not coordinate with metal ions. There are also seen the bands of asymmetric and symmetric carboxylate stretching group vibrations, ν_{asCOO-} *and* ν_{sCOO-}, at 1690, 1680 and 1680 cm^{-1} and at 1296, 1328 and 1340 cm^{-1}, respectively (Tab. 3). It suggests that only one carboxylate anion coordinates with central ion. In the spectra of complexes the C=C stretching vibration bands, ν(C=C), and C–H scissoring vibration bands, δ(C–H), are in the ranges of 1104 – 1088 cm^{-1} and 756 – 748 cm^{-1}, respectively.

There are some new bands present in the spectra of compounds not being seen in the ligand IR spectrum. The bands at 680 – 580 cm^{-1} confirmed the presence of the metal ion–oxygen bonds in complexes[38,39]. Their various frequency values may suggest the different stability of M–O bonding. The M–N stretching vibration bands, ν(M–N), in the IR complex spectra appearing at 488 – 416 cm^{-1} indicate the ion metal coordination with nitrogen atom[40,41].

There are the differences between the spectrum of ligand and the spectra of its compounds. In the spectra of complexes are bands at 3440 – 3332 cm^{-1}, characteristic for ν(OH) stretching vibrations confirming the presence of water molecules in the compounds. These bands are not in the ligand spectrum. Ketonic bands of indole C=O stretching vibrations, ν(C=O), in the spectra of compounds occur in the range of 1725 – 1704 cm^{-1}, while in the H_2L spectrum it appears at 1710 cm^{-1}. The different values of those band frequencies may suggest the C=O group coordination with metal ions in the complex molecules[34,35]. A band due to azomethine nitrogen stretching vibration, ν(HC–N), occurs at 1484 cm^{-1}
in the ligand spectrum whereas in all the complex spectra it is observed only at 1468 cm^{-1}. Therefore, azomethine nitrogen was found to coordinate with metal ions.

In the spectrum of ligand and in the spectra of compounds the bands resulting from C=N and C=C, stretching vibrations, ν(C=N), ν(C=C), and C–H scissoring vibrations δ(C–H), occur at 1620, 1104 – 1088 and 756 – 748 cm^{-1}, correspondingly.

3.5. Magnetic measurements

The magnetic susceptibility of Mn(II), Co(II), Ni(II) and Cu(II) compounds was measured in the ranges of 77 – 303 K and 2 – 300 K.

The effective magnetic moment values experimentally determined in the range of 77 – 303 K changed from: 4.24 to 4.34 μ_B for Mn(II), 3.05 – 3.25 μ_B for Co(II), 3.09 – 2.65 μ_B for Ni(II) and 1.21 to 1.47 μ_B for Cu(II) complexes while those at 2 – 300 K varied from: 3.09 to 5.02 μ_B for Mn(II), 2.22 to 3.12 μ_B for Co(II), 3.12 to 3.87 μ_B for Ni(II), 0.79 to 1.31 μ_B for Cu(II) complexes. The molar susceptibility measurements for helium temperatures were carried out in an applied magnetic field of 0.1 T.

All analysed compounds demonstrate paramagnetic properties and obeyed the Curie–Weiss law. Their magnetic susceptibility values decreased with increasing temperature[42-48]. The dependences of magnetic susceptibility, χ_m^{corr}, its reciprocal values and also $\chi_m^{corr}*T$ worths as a function of temperature for Mn(II) and Cu(II) complexes are presented in Figs. 7 and 8.

At a high temperature region, the magnetic moment values approached the theoretical values Tab. 4. They seem close to spin only values which were calculated at room temperature from the equation $\mu_{\text{eff}}=[4s(s + 1)]^{1/2}$ for Mn(II), Co(II), Ni(II) and Cu(II) ions and are equal to 5.92; 3.88; 2.83 and 1.73 μ_B, respectively.

The obtained data indicated that there is no significant orbital contribution to the magnetic moments of the complex, or its contribution may be essential.

Values of μ_{eff} = 3.09 – 5.02 μ_B for Mn(II) compound may suggest that it is high-spin compound with weak ligand field[42–43] and its sp^3d^2 hybridization[44]. The electronic configuration in this case for Mn(II) ion is $t_{2g}{}^3e_g{}^2$. The magnetic moment values changed from 3.09 μ_B (at 2 K) to 5.02 μ_B (at 300 K). At 300 K the $\chi_m \cdot T$ value is equal to 3.1416 cm^3 K mol^{-1} (Fig. 7). With a lowering of a temperature its value decreases to 2.6774 cm^3 K mol^{-1} (at 43.35 K) which perhaps results from the antiferromagnetic interaction between the magnetic centres of complex. At the temperature values lower than 43.35 K, the worths of $\chi_m \cdot T$ drastically decrease to 1.1914 cm^3 K mol^{-1} (at 2 K). It indicates the antiferromagnetic interaction around magnetic centres as well. The values of magnetic moments are lower than that theoretically calculated. Probably the vectors L and S are aligned by the strong field of the heavy atom in opposite directions which diminishes the resultant magnetic moment. The analysed Mn(II) complex seems high – spin with octahedral symmetry of Mn(II) ion. In the coordination sphere of Mn(II) ion may be four oxygen atoms, two of them coming from monodentate carboxylate groups, two others from indole groups and there are also two nitrogen atoms of azomethine groups. However due to the lack of crystallographic data this interpretation seems rather speculative based only on magnetic moment values and IR spectra data interpretations.

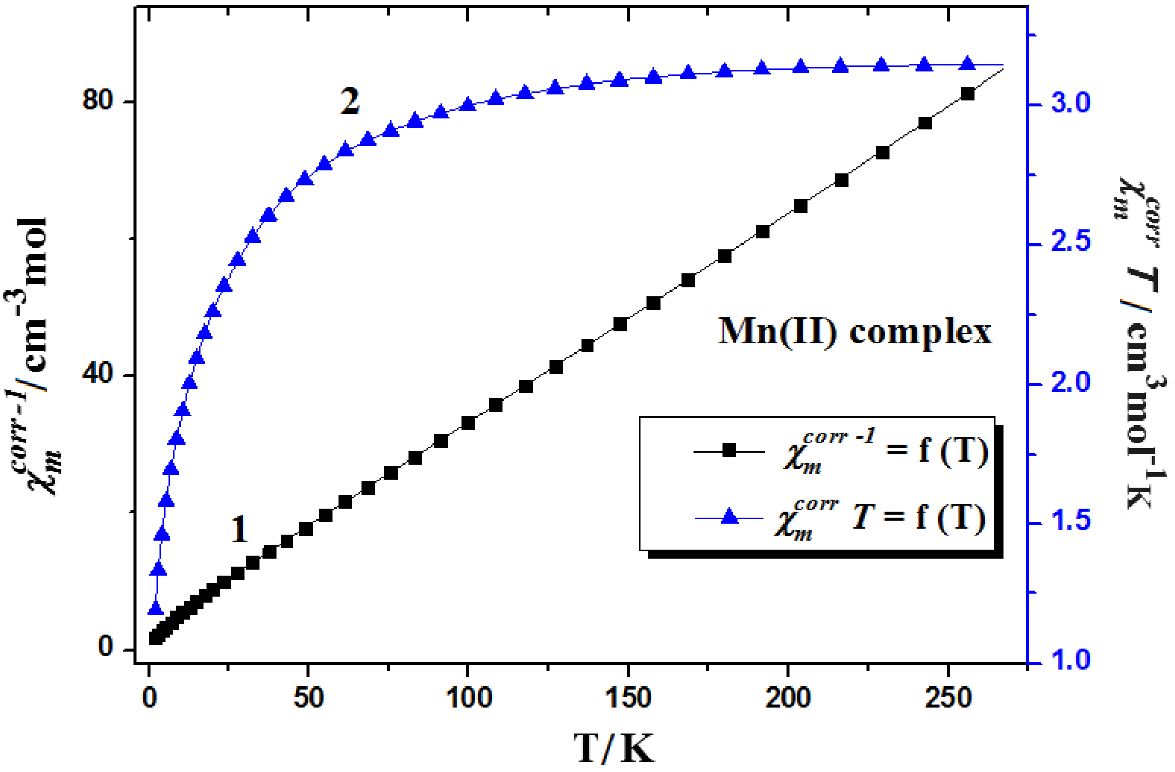


Figure 7. Dependence of (1) $\chi_m^{corr\text{-}1}$ and (2) $\chi_m^{corr}\cdot T$ values *vs*. *T* for Mn(II) complex.

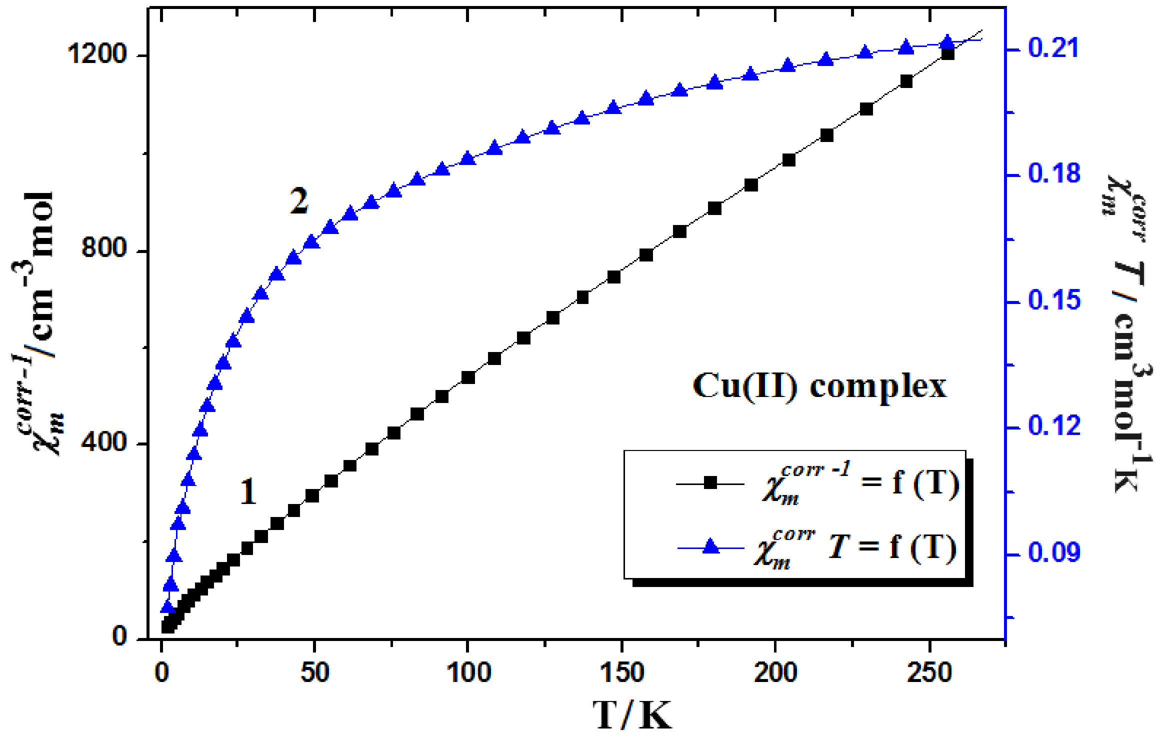


Figure 8. Dependence of (1) $\chi_m^{corr\text{-}1}$ and (2) $\chi_m^{corr}\cdot T$ values *vs*. *T* for Cu(II) compound.

Table 4. The comparison of spin only values of magnetic moments (μ_B) for ions of Mn(II), Co(II), Ni(II), Cu(II) with those experimentally found for their complexes in literature[42-46] and measured in our experiments

	Central atom			
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Number of *d* electrons	5	7	8	9
High–spin complex				
Number of unpaired electrons	5	3	2	1
Spin-only moment (μ_B)	5.92	3.88	2.83	1.73
Magnetic moment (μ_B) literature data	5.32–6.10	4.30–5.20	2.80–3.50	1.70–2.20
Low–spin complex				
Number of unpaired electrons	1	1	0	
Magnetic moment (μ_B) literature data	1.80–2.10	1.80		
Gouy's method experimental data (76-303 K)	4.24–4.34	3.05–3.25	3.09–2.65	1.21–1.47
SQUID–VSM experimental data (2-300 K)	3.09–5.02	2.22–3.12	3.12–3.87	0.79–1.31

For Co(II) complex the values of magnetic moment values changed from 2.22 (at 2 K) to 3.71 μ_B (at 7.88 K) showing magnetic saturation and then with the increasing temperature it changed to 3.12 μ_B (at 300 K). At 300 K the $\chi_m^{corr}\cdot T$ value was equal to 1.2117 cm^3 K mol^{-1} (μ_{eff} = 3.12 μ_B). Upon temperature lowering the $\chi_m^{corr}\cdot T$ and the magnetic moment values at first gradually increase and next evenly decrease to 0.9215 cm^3 K mol^{-1} at 20.8982 K. Next with the cooling of the sample the $\chi_m^{corr}\cdot T$ values increase rapidly, changing their values from 0.9215 to 1.7149 cm^3 K mol^{-1} (at 7.8803 K) reaching the saturation paramagnetic state and gain the magnetic moment value 3.71 μ_B, (Neel temperature). At 7.8803 K the complex shows the paramagnetic properties, while next changing temperature from 7.8803 to 2 K, the $\chi_m^{corr}\cdot T$ values again rapidly decrease to 0.6159 cm$^3\cdot$mol^{-1}. It results from the antiferromagnetic order between Co(II) centres or from the possible intermolecular hydrogen bonds in the compound crystal lattice[49]. This drastic decrease of $\chi_m^{corr}\cdot T$ indicates a negative θ value which may confirm the antiferromagnetic intermolecular interaction. The magnetic moment values are lower compared to that theoretically calculated. The electronic configuration in Co(II) ion under ligand field influence is $t_{2g}^5e_g^2$.

For Ni(II) ion complex the magnetic moments change from 3.12 μ_B (at 2 K) to 3.87 μ_B (at 300 K). At 300 K the χ_mT value is equal to 1.8659 cm^3 K mol^{-1}. With a lowering of a temperature its value increases to 18.4818 cm^3 K mol^{-1} at 8.9516 K and then drastically decrease to 1.7149 cm^3 K mol^{-1} at 2 K. It is connected with antiferromagnetic interactions that occur in Ni(II) centre, (θ has negative sign). At 8.9516 K (Neel temperature) the complex shows the paramagnetic properties. The magnetic moment values are higher than that calculated theoretically which may indicate the ferromagnetic interaction around the Ni(II) ion. These values may suggest the octahedral environment of Ni(II) ion[49]. The electronic distribution in Ni^{2+} cation in the ligand field may be $t_{2g}^6e_g^2$.

For Cu(II) compound the magnetic susceptibility values decrease with rising temperature. The magnetic moment values change from 0.79 μ_B (at 2 K) to 1.31 μ_B (at 300 K). At 300 K the $\chi_m^{corr}\cdot T$ value was equal to 0.2145 cm^3 K mol^{-1} (μ_{eff} = 1.31 μ_B). Upon temperature lowering the $\chi_m^{corr}\cdot T$ and the magnetic moment values decrease very slowly to 0.1622 cm^3 K mol^{-1} (μ_{eff} = 1.14 μ_B) at 45.15 K (Fig. 8). Next their values drastically decrease from 0.1622 cm^3 K mol^{-1} at 45.15 K to 0.0773 cm^3 K mol^{-1} (0.79 μ_B) at 2 K. This sudden decrease could be caused by crystal field effect, as well as the antiferromagnetic interactions between neighbouring 3d metal ions (interaction between magnetic centres of complex) or intermolecular hydrogen bonds in molecular crystal structure[48]. The study of magnetostructural data may indicate that ferromagnetic and antiferromagnetic coupling between adjacent orbitals (d orbitals of the metal ions and the symmetry adapted linear contribution of the ligand orbitals) on Cu neighbouring ions[48]. The magnetic moment values experimentally determined for Cu(II) compound are lower than that theoretically calculated (μ_{eff} = 1.73 μ_B). This may suggest a bidentate character of carboxylate group. However, this formulation seems rather uncertain because of the lack of crystal data. The coordination sphere may have the shape of a trigonal pyramid with one nitrogen and three oxygen atoms in its corners. Two oxygen atoms derived from carboxylate groups from glutamic acid part and third one from indole group of isatin ring. The apex of the pyramid forms a nitrogen atom from the azomethine group. The complex may have a tetragonal geometry around Cu(II) ion[49].

4. Conclusions

The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions form hydrates with 2-(2-oxoindolin-3-ylideneamino)pentanedioic acid anion containing from 1 to 3 water molecules. The compounds are crystalline. The compounds of Mn(II), Co(II), Cu(II) and Zn(II) crystallize in monoclinic while that of Ni(II) in triclinic systems.

Their thermal stability was studied in air at 293 – 1173 K. The complexes are decomposed in three steps. First, they dehydrate in one step releasing all water molecules and form anhydrous compounds to be next decomposed to the oxides of appropriate metals. The enthalpy values of dehydration processes were determined as well. With the rise of temperature, the hydrates release the water molecules the presence of which in the gaseous mixture was confirmed by the bands in the range of 4000–3600 and 1700–1400 cm^{-1}. During heating the complexes being decomposed release the CO_2, CO, hydrocarbons gaseous molecules, the presence of which in the gaseous mixture was identified by FTIR spectra. The magnetic susceptibility of complexes was investigated in the ranges of 77 – 303 K and 2 – 300 K. All of them obey Curie-Weiss law showing the paramagnetic properties. In the molecular central ion, the ferromagnetic or antiferromagnetic interactions occur.

From the obtained results it appears that in Co(II) and Cu(II) complexes two carboxylate groups take part in the metal ion coordination while in those of Mn(II), Ni(II) and Zn(II) only one carboxylate anion coordinates to central metal. The second carboxylic group does not coordinate with central ions.

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Hydrodeoxygenation and pyrolysis of free fatty acids obtained from waste rendering fat

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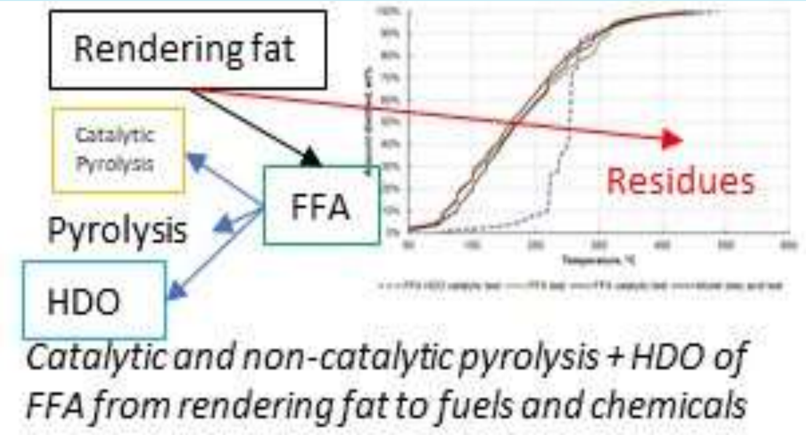
ABSTRACT: Non-edible fats are a common renewable feedstock for the biofuels production to avoid partially the use of edible feeds and fossil fuels. The aim of this work was the use of waste rendering fat to produce pyrolyzed and hydrogenated oils. The feedstock was hydrolyzed producing free fatty acids and glycerol + residues. The free fatty acids were pyrolyzed (with and without metal sulfides metal supported catalyst) or hydrotreated separately. An autoclave closed hermetically in nitrogen (pyrolysis) or hydrogen (hydrotreatment) atmosphere was used. Gaseous products were analyzed by GC-FID/TCD. Liquid products were analyzed by Simulated Distillation (ASTM D2887) and FT-IR (attenuated total reflectance technique). For the pyrolysis, the main gaseous products were carbon dioxide, methane, ethane, and propane. For the hydrotreatment, the total amount of gases produced was much lower being the main product the carbon dioxide. For liquids, the hydrotreatment of the free fatty acids produced the respective hydrocarbons by decarboxylation reaction and the pyrolysis produced a mixture of compounds with lighter boiling ranges compared to the original free fatty acids. The use of a metal sulfide metal supported catalyst in the pyrolysis led to a higher amount of hydrogen production. but similar boiling range liquid products compared to the non-catalytic test.



1. Introduction

The petroleum location in unstable territories, the fossil fuel restrictions by law and the greenhouse carbon dioxide production led to a high need in biofuels production. Concretely, the revised Renewable Energy Directive (EU) 2018/2001, adopted in December 2018 by the European Parliament and by the Council of Ministers of the European Union, promotes the use of energy from renewable sources in the European Union. In addition, the European Union is avoiding the use of croplands for the biofuels production. In 2015 new rules came into effect to reduce the risk of indirect land use change (Renewable Energy Directive 2009/28/EC and the Fuel Quality Directive 2009/30/EC). Therefore, the use of wastes to produce biofuels can be considered as a necessary alternative for the biofuels production.

Three types of biofuels are considered worldwide: (i) first-generation biofuels (conventional ones such as fatty acids methyl esters – FAME), (ii) second-generation biofuels are produced from non-edible raw materials and can be produced by catalytic hydrotreatment and (iii) third-generation biofuels products from algae feedstock[1]. In the case of cold weather countries, the using of first-generation biofuels (biodiesel) can be a problem because they present a high freezing point or low energy density (due to its oxygen content). Second-generation biofuels are nowadays produced, in refineries, by catalytic hydro-processing to obtain hydrocarbons[2-5]. Particularly, non-edible feedstocks are being using in refineries[6]. Concretely, the use of waste animal fat[1,7] is considered as a good option for the biofuels production. Third-generation biofuels can be considered as a key technology. However, this technology needs to be still improved and implemented (not yet used on an industrial scale)[8].

Rendering fat (RF) is a non-edible waste feedstock which can be produced from the waste of slaughterhouses and carcasses of livestock and it is considered as a cheap material for green diesel production[9]. However, RF contains usually high phosphorous and metal contents which could affect the catalytic activity[9]. RF is produced in Czech Republic in a relatively large amount so it can be considered as an available and cheap feedstock in this zone-area[10]. The amount registered of rendering fat, sludge, meat and bone meals residues produced in Czech Republic (2018) were 36780 tons all together[11]. The lipid wastes generated by commercial enterprises in Czech Republic (2017) classified by groups were the next: Spent waxes and fats 1640 tons, waste fats and oils 21979 tons, edible fat, and oils 2971 tons and other greases and oil mixtures 374 tons[12].

Biofuels of second generation can be obtained by hydrodeoxygenation (HDO) or by pyrolysis. The pyrolysis is an extensively studied pathway to convert triacylglycerols to hydrocarbons. However, the study of pyrolysis for free fatty acids has received lower attention[13,14]. The aim of this work was to evaluate the free fatty acids (from rendering fat) processing by catalytic and non-catalytic pyrolysis to fuels and chemicals using metal sulfide supported catalyst and compare these results with standard hydrodeoxygenation (HDO) process by using the same catalyst. NiW sulfide supported on SiO_2-Al_2O_3 is a commercial catalyst. This material was used instead standard NiMo or CoMo (used standardly for HDO reactions) supported catalysts with the added aim of cracking the free fatty acids to shorter molecules producing gases, gasoline and diesel fractions which could be then be evaluated for being used for fuels or petrochemistry.

2. Experimental

2.1. Materials

Waste RF (from dead animals, pig (80 wt.%) also including chicken (14 wt.%) and cow (6 wt.%) residues) used in a previous work[7] was analysed (metal and elemental C, H, N, S analyses) as shown in Tab. 1.

Table 1. Metals and elemental C, H, N, S, O% (oxygen calculated by difference) and ash composition for the RF.

Metal composition	Amount	Units
Al	<0.4	mg kg^{-1}
Ca	110	mg kg^{-1}
Cr	6.38	mg kg^{-1}
Fe	13.3	mg kg^{-1}
K	218	mg kg^{-1}
Mg	16.6	mg kg^{-1}
Mn	<0.2	mg kg^{-1}
Na	216	mg kg^{-1}
Ni	<0.2	mg kg^{-1}
P	50.1	mg kg^{-1}
Ti	<0.2	mg kg^{-1}
C	76.6	wt.%
H	12.3	wt.%
S	--	mg kg^{-1}
N	800	mg kg^{-1}
Oxygen by difference	11.0	wt.%
Ash content[1]	0.3	wt.%
Acid value[2]	65.5	mg KOH g^{-1}
Water content	2650.3	mg kg^{-1}

[1]The ash content was calculated by TGA in Oxygen from 50 to 900 °C, 10 °C min^{-1}.

[2]Milligrams of KOH added to 1 g of RF to obtain pH = 7.

Oleic acid Lach-ner (Oleic acid min. 70% pure/1000 ml; CAS: 67701-08-0; EINECS: 266-932-7; Assay fatty acids (as oleic acid) min. 97%; Refractive index 1.460 - 1.463) was used as model molecule for pyrolysis.

Dimethyl disulfide (DMDS) ≥ 99.0% Sigma Aldrich was used for the commercial catalyst sulfidation. NiW/SiO_2–Al_2O_3 reference material as catalyst with a 6.4 and 17.5 wt.% of Ni and W contents respectively (200 m^2 g^{-1} of BET surface) was tested.

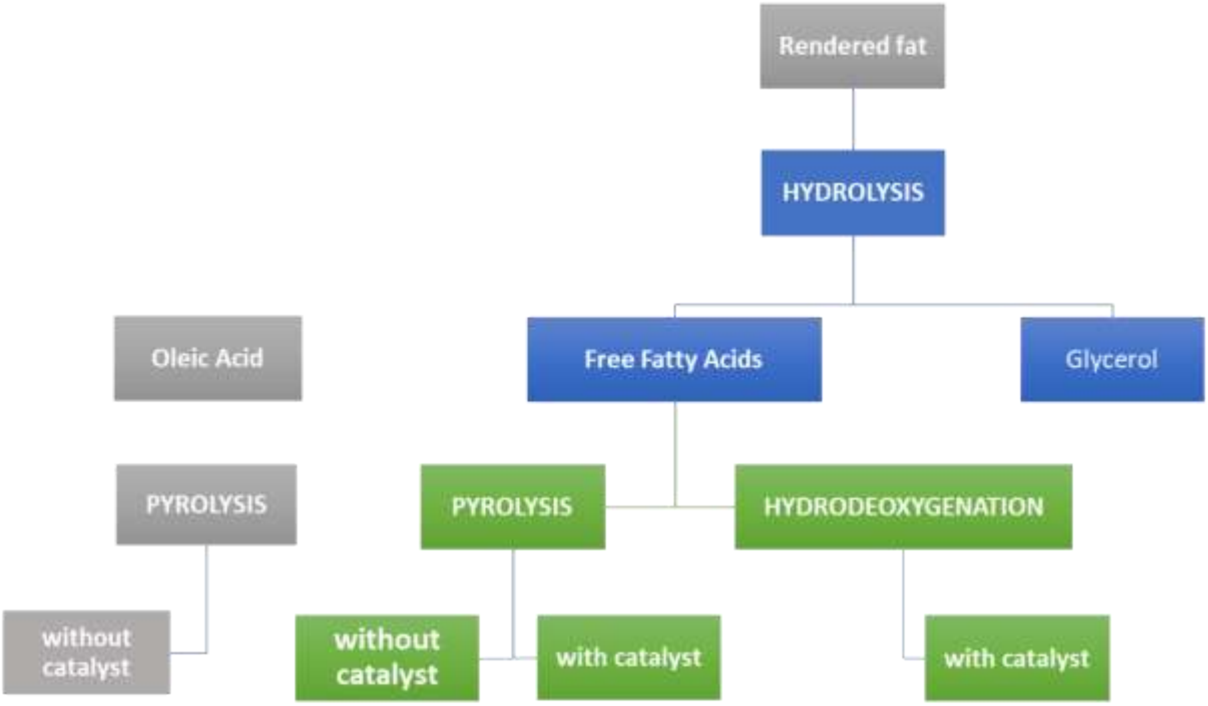


Figure 1. Scheme of the work-process using RF as feedstock for hydrolysis to FFA and then pyrolysis and HDO. Oleic acid was used as model molecule.

2.2. Tests

Experiments were performed in an autoclave 4575/76 with a “4848B” controller delivered by Parr Instruments Company. The scheme of the overall work-process is exposed in Fig. 1. The catalyst was activated using DMDS. 20 g of DMDS and 5 g of catalyst were used for each activation. DMDS and catalysts were introduced into the reactor-autoclave. Then, the reactor was flushed with nitrogen to remove air residues and finally flushed and pressurized to 5 MPa with hydrogen. Temperature was then increased from ambient temperature (24 °C) to 340 °C with a rate of 8.3 °C min^{-1}. At this temperature (340 °C), the pressure was increased to 15 MPa (by H_2 flow) and the reactor was kept at these conditions for 1 h. The activation period was followed by the reactor external cooling by air flow (cooling rate approx. 4.5 °C min^{-1}) to ambient temperature and stabilization for 1 h.

For hydrolysis of rendering fat, HDO and pyrolysis tests similar procedures were performed. Three types of tests were carried out:

A) For hydrolysis, two tests were performed, 50 g of rendering fat, 50 g of distilled water and 2 g of sulfuric acid were used. The reactor was under nitrogen atmosphere with no added pressure. Then, it was heated to 250 °C and maintained at this temperature during 1 h with 500 rpm of stirring rate. After reaction, the system was externally cooled by air flow (approx. 4.5 °C min^{-1}) to room temperature and stabilized for 20 h. After that, the liquid was collected for analysis. After the hydrolysis the glycerol was considered as side product while free fatty acids were further processed in two ways: in a pyrolysis or in HDO reaction.

B) For pyrolysis, 18.4 g of free fatty acids (FFA) and 3.7 g of activated-sulfide NiW/SiO_2-Al_2O_3 catalyst were used. The autoclave was tested in nitrogen with no added pressure at room temperature and then heated to 420 °C with a heating rate of 8.3°C min^{-1}. Reaction was conducted stirring with a rate of 500 rpm. Then, the system was externally cooled. Afterwards, the gas was sampled at 30 °C and the autoclave depressurized. After that, the autoclave was opened, and the liquid collected for analysis. A blank probe, with 20 g of FFA and without the use of a catalyst and pyrolysis with oleic acid as a model molecule was also done, according to the above described procedure.

C) For HDO reaction, 20 g of FFA and 5 g of sulfide NiW/SiO_2-Al_2O_3 commercial catalyst were placed in the autoclave. The reactor was then flushed with nitrogen and pressurized with hydrogen to 7 MPa. Then, the reactor was heated up to 365 °C. The system was maintained at 365 °C for 1 h and stirred with 500 rpm. The, the system was cooled, and gas sampled at 30 °C. Finally, the autoclave was depressurized and opened for collecting the liquid.

2.3. Products analyses

Liquid products of the reaction were characterized by simulated distillation (SimDist) using gas chromatography according to the ASTM D2887 and attenuated total reflectance FT-IR technique (ATR). Gaseous products were analysed by RGA-GC (Method Refinery Gas Analysis, Agilent).

3. Results and Discussion

First, the hydrolysis of the RF was performed. The hydrolysis of triglycerides (Triglyceride + 3 $H_2O \rightleftharpoons$ 3 Fatty Acids + Glycerol), in the presence of water, produces free fatty acids and glycerol (the sulfuric acid addition led to the acid hydrolysis). In this case, the hydrolysis reaction was carried out not only to produce free fatty acids and separate them from the glycerol but also to remove other possible water-soluble compounds included previously in the original rendering fat (not triglycerides).

Two tests with similar results (Tab. 2) were carried out. The simulated distillation of the FFA product presented about 90 wt.% of pure FFA (Fig. 2). After hydrolysis tests no gaseous samples (C1-C4 gases) were produced. Glycerol and organic phases were separated by centrifugation. The organic phase SIMDIS is shown in Fig. 2.

The main products in the organic phase were FFA as shown in Fig. 2 (boiling range 340 – 420 °C). The SIMDIS was calibrated and as shown in a previous work[7], the boiling range of 50 – 220 °C is related to C5-C12 compounds, 220-340 °C to C12-C19, 340-420 °C is mainly related to the free fatty acids but also to C20 + compounds and > 420 °C is related mainly to mono, di and triglycerides. Then, these FFA were used as feedstock for pyrolysis.

Table 2. Amount of liquid, gaseous and residue products obtained.

Reaction	Liquid (wt.%)	Gas (wt.%)
Hydrolysis of rendering fat 1.	71.72	28.28 (no gases, residue)
Hydrolysis of rendering fat 2.	71.67	28.33 (no gases, residue)
FFA test in nitrogen without catalyst	64	36
FFA catalytic test in nitrogen	79.64	20.36
Oleic acid test in nitrogen without catalyst	82.5	17.5
Hydrodeoxygenation of FFA with catalyst	94.8	5.2

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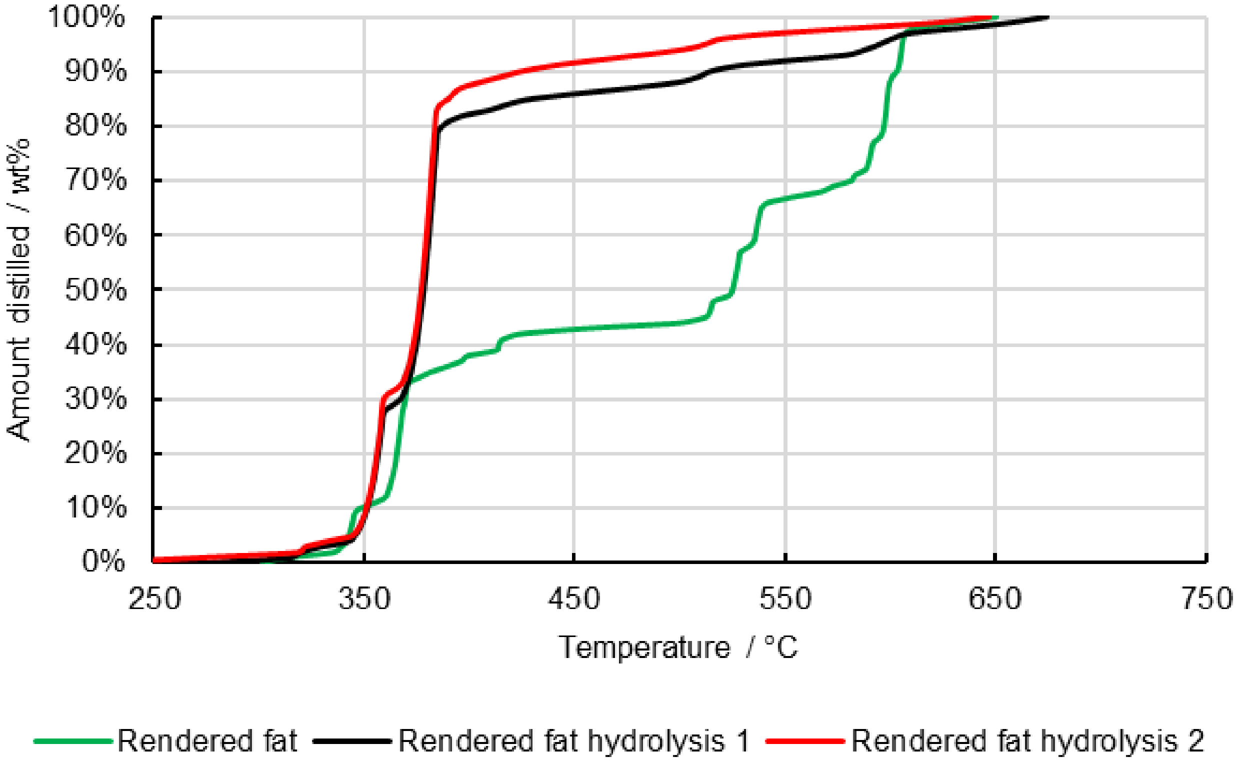

Figure 2. Simulated distillation of rendering fat and hydrolysis products.

Next, after obtaining the FFA, two tests were carried out with FFA. One test using sulfide commercial catalyst and one test without catalyst. Oleic acid was also used as model molecule to perform a pyrolysis test for comparing results with those obtained using FFA from RF.

The pyrolysis led to an effective conversion to liquid and gaseous products different than feedstock as shown in Fig. 3. The SimDis and RGA analyses together demonstrated that the pyrolysis was effective producing lighter products compared to the free fatty acids (FFA) due to a cracking process. As shown in Tab. 2, the use of a sulfide catalyst increased the light liquid production and decreased the number of gaseous products C1-C6. The amount of gases and liquids compared between FFA and oleic acid tests are different due to the presence of other FFA in the animal fat (not only oleic acid). HDO test clearly led to hydrocarbons (Fig. 3) especially to products C15-C18 according to calibrated RGA methodology peaks. This result is confirmed by ATR (Fig. 4) not showing signals for oxygenated compounds.

The gaseous products composition is shown in Fig. 5. The use of catalyst in nitrogen tests produced an increment in the hydrogen composition in gas products. Thus, the use of a sulfide catalyst led to a higher amount% of hydrogen in the product but a total less amount of gases as consequence of the higher production of carbon dioxide in nitrogen tests. In the case of the oleic acid, the amount% composition is similar to the FFA test without catalyst in nitrogen. So, the gasification activity was similar in selectivity but different in the total production of gases. The total production of gases could be favored by the other compounds present in the animal fat.

HDO test clearly showed four main increments of the amount distilled at 270, 286, 305 and 318 °C which are related to C15-C18 hydrocarbons, respectively. Two significative increments of amount distilled were also shown for catalytic FFA pyrolysis tests (C15 and C17 hydrocarbons zone) indicating that the use of the metal sulfide catalyst led to a higher amount of C15, C17 hydrocarbons. However, in pyrolysis no hydrogen was used so these hydrocarbons could be produced by the hydrogen produced by the initial FFA hydrogen loss originated during the test.

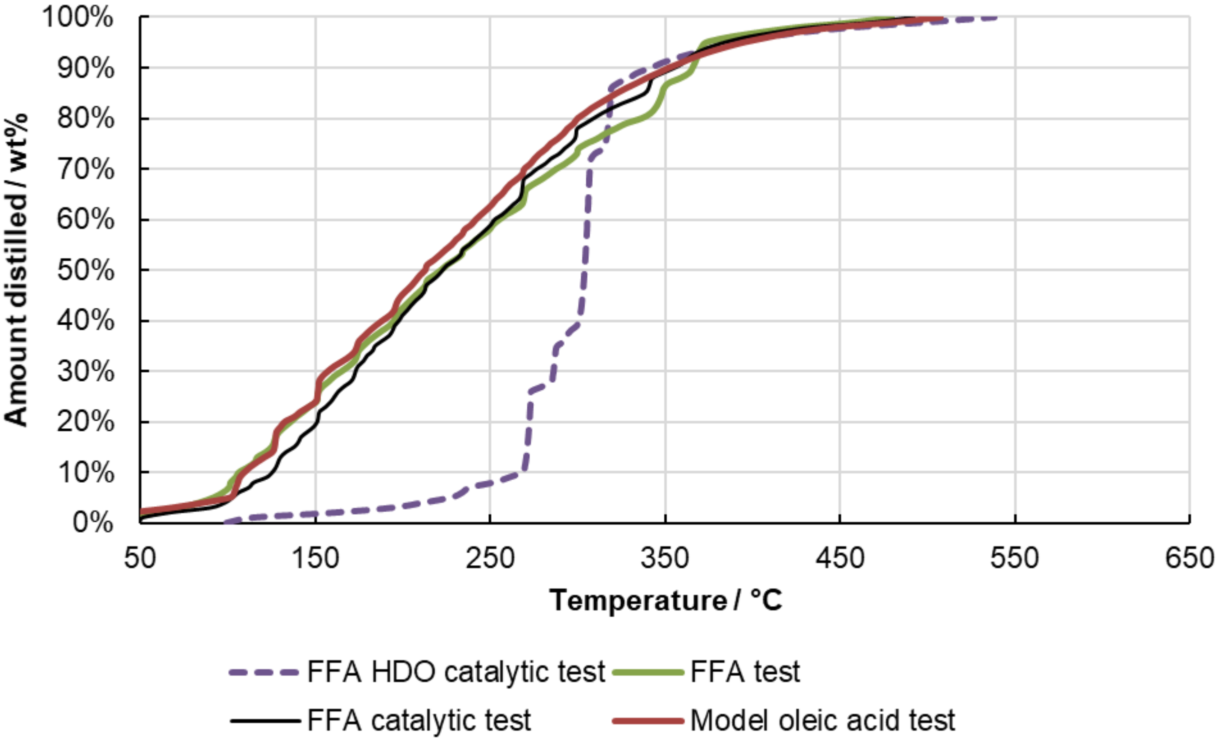

Figure 3. SimDis of liquid products from tests using nitrogen and for HDO test. The reaction was conducted without catalyst in nitrogen (FFA and Model oleic acid tests), with sulfide catalyst (FFA HDO catalytic test and FFA catalytic test).

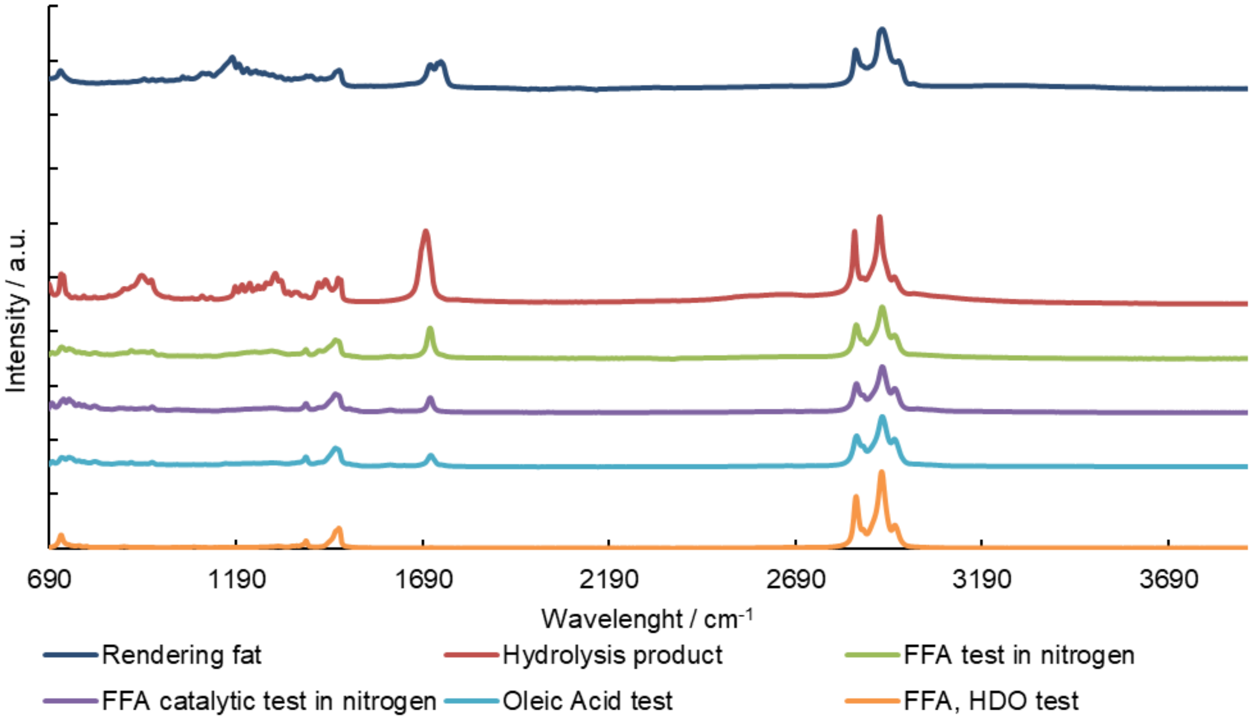

Figure 4. ATR spectrum of all feedstocks and reaction products in this experiment.

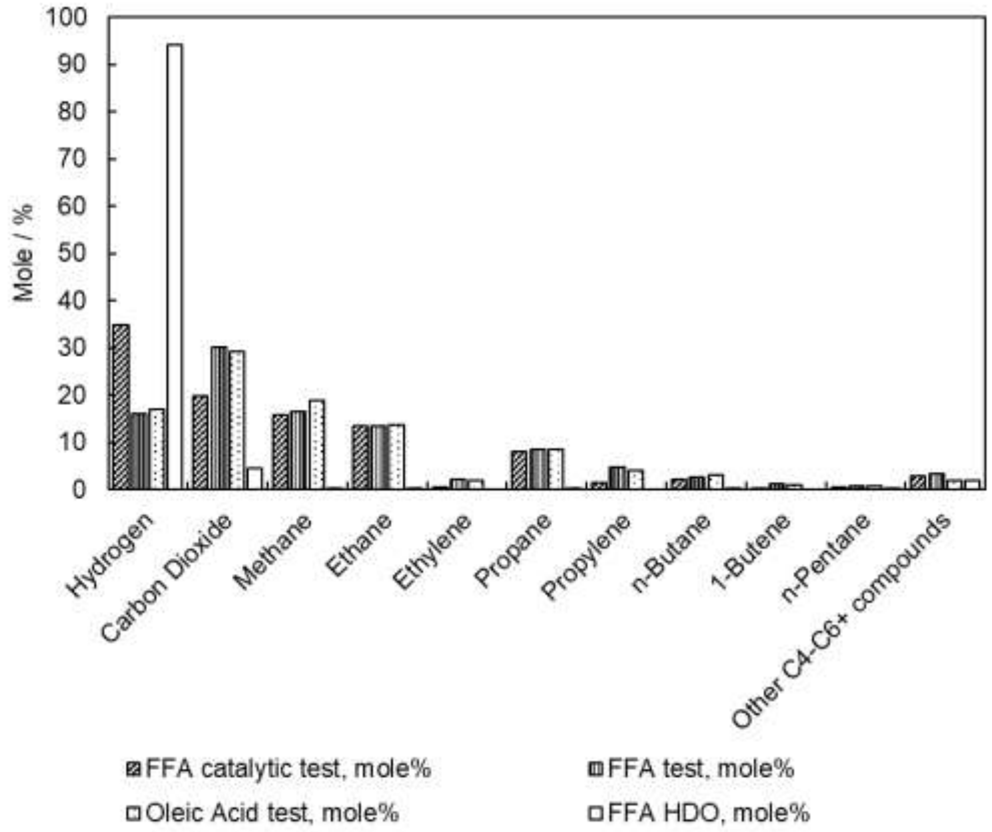

Figure 5. RGA gases analysis for pyrolysis and HDO tests.

ATR absorbance spectra of liquid products in the frequency range between 690 and 4000 cm^{-1} are shown in Fig. 5. In general, for triglycerides and hydrogenated vegetable oils, the bands at 2925, 2965 cm^{-1} are related to the stretching vibrations of the CH_3 and CH_2 groups[14]. The absorption at 3100–3000 cm^{-1}, 1603 cm^{-1}, 1500 cm^{-1} and 900–700 cm^{-1} is typical for aromatic compounds[14]. The band at 1709 cm^{-1} can be attributed to the presence of free fatty acids and the band at 1746 cm^{-1} to the ester carbonyl functional group of the triglycerides which was only present in the feedstock[14]. Concretely, the band at 1746 cm^{-1} was only found for the feedstock confirming the hydrolysis of the animal fat to FFA. However, for the feedstock and hydrolysis products, the band at 1182 cm^{-1} can be attributed to the stretching vibration of the C-O ester groups indicating a non-complete hydrolysis being this result in agreement with SimDis (amounts distilled at higher temperatures than 420 °C). At 727 cm^{-1} was found a band attributed to the overlapping of the CH_2 rocking vibration and the out-of-plane vibration of cis-disubstituted olefins[14]. The shoulder at 2890-3009 cm^{-1} C-H (stretching vibration of the cis-double bond (=CH)) found for the feedstock was also present in the liquid products.

Although the pyrolysis and HDO reaction of oleic acid and rendering fat were already studied[15-18], to the best of our knowledge, comparing with literature, a comparison between non-catalytic and catalytic pyrolysis of rendering-fat using sulfide catalyst was not found. In addition, the use of oleic acid led to know the possible differences by using real feedstock and this model molecule.

4. Conclusions

Several tests of hydrolysis, HDO and pyrolysis were performed obtaining good yields to free fatty acids (hydrolysis) and hydrocarbons (HDO). Pyrolysis tests of FFA were carried out with and without catalyst to see its influence. The use of catalyst led to an increment in hydrogen production, decrease in total gas production and to higher amounts of C15 and C17 hydrocarbons compared to non-catalytic pyrolysis. Lighter olefins, aromatics and hydrocarbons were produced after pyrolysis.

5. Acknowledgment

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Determination of paracetamol in pharmaceutical samples by spectrophotometric method

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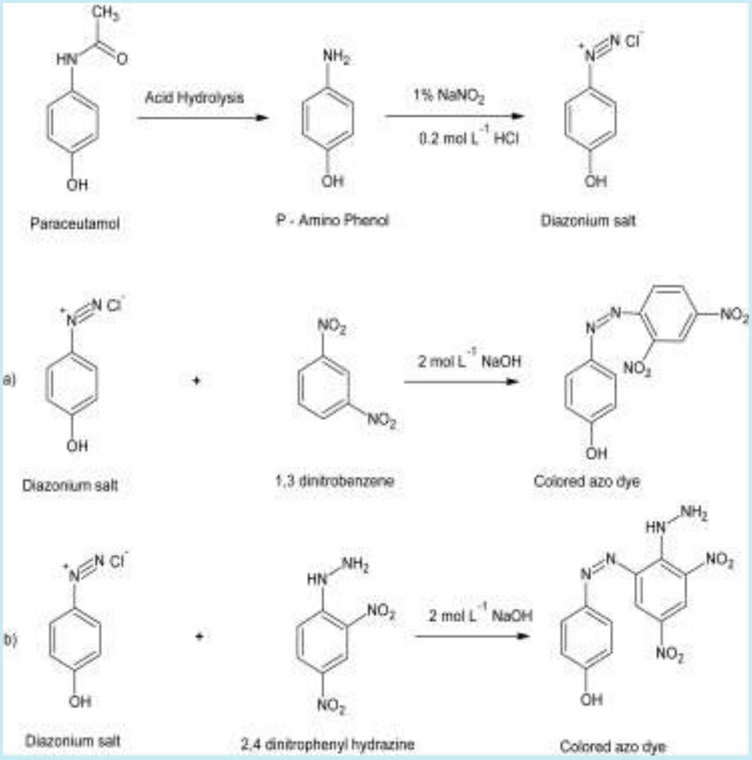
ABSTRACT: It is described the use of 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine is used as coupling agent for the spectrophotometric determination of paracetamol. This method is easy and simple based on the reaction of acid hydrolysis of paracetamol to produce p-aminophenol, which in turn reacts with nitrite in acidic standard to form diazonium ion, which is coupled with coupling agent in basic standard to produce azo dyes. The formed dyes follow Beer's law in the range of 0.8-20.5 µg mL^{-1} of paracetamol with 1, 3 dinitrobenzene or 0.5-18.4 µg mL^{-1} of paracetamol with 2,4 dinitrophenyl hydrazine with absorption maxima at 429 nm or 430 nm. The molar absorptivity and Sandell's sensitivity of paracetamol with 1,3 dinitrobenzene or paracetamol with 2,4 dinitrophenyl hydrazine azo dyes were 1.965×10^4 L mol^{-1} cm^{-1} or 2.776×10^4 L mol^{-1} cm^{-1}, and 7.692×10^{-3} µg cm^{-2} or 5.698×10^{-3} µg cm^{-3} respectively. The dyes formed are stable for more than 12 h. The optimal reaction circumstances and other analytical parameters are evaluated. Interference due to foreign organic compounds have been studied. The method has been effectively applied to the determination of paracetamol in pharmaceutical samples.



1. Introduction

Paracetamol called acetaminophen or 4-acetamidophenol, is a common pain reliever and fever reduction medicine[1]. Its chemical name is N-acetyl-p-aminophenol with a chemical formula $C_8H_9NO_2$. Paracetamol was first prepared in 1878 by Harmon Northrop Morse an American chemist[2]. It is available as a generic medication with trade names including Tylenol and Panadol, among others[3]. It is often sold in the commercial markets with a major ingredient in many cold and flu remedial combination drugs. It is usually used either by mouth or rectally, but is also available intravenously[1,4]. Paracetamol is accessible in as a tablet, drops, capsules, injection, and syrup[5].

Paracetamol is usually safe at suggested doses[6]. The suggested maximum daily dosage for an adult is 3 or 4 grams[7,8]. Higher doses may result in toxicity, including liver disaster. Serious skin rashes may infrequently occur, and it appears to be secure during pregnancy and breastfeeding[1].

Paracetamol is also used for severe ache, such as cancer ache and ache after surgery, in combination with opioid ache medication[9]. Paracetamol has a highly targeted action in the brain, blocking an enzyme involved in the transmission of ache. Its mode of action was known to be different compared to other pain relievers, but although it produces pain relief throughout the body[10]. It is on the WHO's List of essential medicines, the most effective and safe medicines desired in a health system[11].

A lot of techniques are existing in the literature for the determination of paracetamol in various types of pharmaceutical preparations. These techniques are titrimetric[12], HPLC and RP-HPLC[13-15], HPTLC[16], Voltametric[17-20], electrochemical[21] and spectrophotometry[10]. Several spectrophotometric techniques for the determination of paracetamol are presented in the literature[10,22-41].

The reagents reported for the spectrophotometric determination of paracetamol are less selective, less sensitive and some require stringent experimental conditions and are chronic toxic in nature[27,33,36,38]. The present research work is on spectrophotometric determination of paracetamol in pharmaceutical samples. The hydrolyzed product of paracetamol is diazotized with nitrite in acidic standard at room temperature and the diazonium salt thus shaped is coupled with 1,3 dinitrobenzene and 2,4 dinitrophenyl hydrazine to give colored azo dye in alkaline standard is the source for the determination of paracetamol. The method has been successfully applied to the determination of paracetamol in pharmaceutical samples.

2. Experimental

2.1 Instruments used

A SHIMADZU Deutschland GmbH UV-2550 spectrophotometer and a pH meter- WTW pH 330 were used.

2.2 Chemicals and reagents used

Stock solution of paracetamol (Gift sample from Matrix Laboratory, Hyderabad, India): Weighed an amount 0.251 g of paracetamol and was dissolved in 10-15 mL of ethanol then the solution is transferred into a 250 mL standard flask, fulfilled to the mark with double distilled water (1000 µg mL^{-1}). Working solution was prepared as required by dilution.

Sodium nitrite solution (0.5%), hydrochloric acid solution (0.5 mol L^{-1}), 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine solution (2%), sodium hydroxide solution (2 mol L^{-1}).

2.3 Hydrolyzed paracetamol solution (100 µg mL^{-1})

A 150 mL of 1000 µg mL^{-1} paracetamol solution was transferred to 250 mL round bottomed flask provided with 20 mL of 4 mol L^{-1} of hydrochloric acid, then refluxed for 1 h, kept aside to cool the solution, then neutralized with 20% of sodium carbonate solution, then diluted with distilled water using a 250 mL volumetric flask. A 16.6 mL of the above solution was diluted with distilled water in a 100 mL volumetric flask to prepare 100 µg mL^{-1} paracetamol[40].

2.4 Paracetamol tablets solution (1000 µg mL^{-1})

Paracetamol tablets of different trademarks were purchased from local pharmacy and were finely powdered. An accurately weighed amount of powder equivalent to 0.25 g paracetamol was dissolved in 10-12 mL ethanol, then 90-100 mL distilled water was added, mixed well to increase the solubility, filtered into 250 mL calibrated flask. Then the solution was completed to the mark with distilled water, and progress as mentioned above in preparation of hydrolyzed paracetamol solution[40].

2.5 Paracetamol tablets of different trademarks used

P-750: 750 mg. Apex Laboratories Pvt. Ltd. Chennai, TamilNadu, INDIA, Dolopar: 650 mg. Micro LabsLtd. Bangalore, INDIA, Disprin Paracetamol: 500 mg. Reckitt & Benckiser Ltd. Gurgaon, Haryana, INDIA, Crocin Quik: 500 mg. Glaxo Smithkline, Mumbai, Maharashtra, INDIA, Paramet: 500 mg. Wallace Pharmaceuticals Ltd. Goa, INDIA, Nicetamol: 125 mg. Dr. Reddy's Laboratories Ltd, Hyderabad, Andra Pradesh, INDIA, Paracip 500 mg. Cipla Limited, Mumbai, Maharashtra, INDIA.

2.6 Procedure for the determination of paracetamol

An aliquot of the solution containing paracetamol (μg mL^{-1}) was transferred into a string of 10 mL calibrated flasks. Add 1 mL of 0.5% solution of $NaNO_2$ and 0.5 mL of 0.5 mol L^{-1} HCl and then the solution was mixed thoroughly and kept away for accomplishment of diazotization reaction. Then, add 1 mL of 2% 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine and 1.5 mL of 2 mol L^{-1} NaOH solutions and then diluted to 10 mL, using distilled water, and mixed thoroughly. Later the absorbance of the colored azo dye formed was measured at 429 nm or 430 nm beside the reagent blank.

3. Results and Discussion

The diazotization of paracetamol with nitrite, followed by the coupling of 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine in alkaline standard. The absorption spectra of the azo dye produced between paracetamol-1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine is presented in Fig. 1 having absorption maximum at 429 nm or 430 nm, respectively. The plot of absorbance against concentration of paracetamol coupled with 1, 3-dinitrobenzene or 2,4 dinitrophenyl hydrazine is presented in Fig. 2. The formed dyes obeys Beer's law in the range of 0.8-20.5 μg mL^{-1} of paracetamol with 1,3 dinitrobenzene or 0.5-18.4 μg mL^{-1} of paracetamol with 2,4 dinitrophenyl hydrazine and the reaction method is shown in Scheme 1.

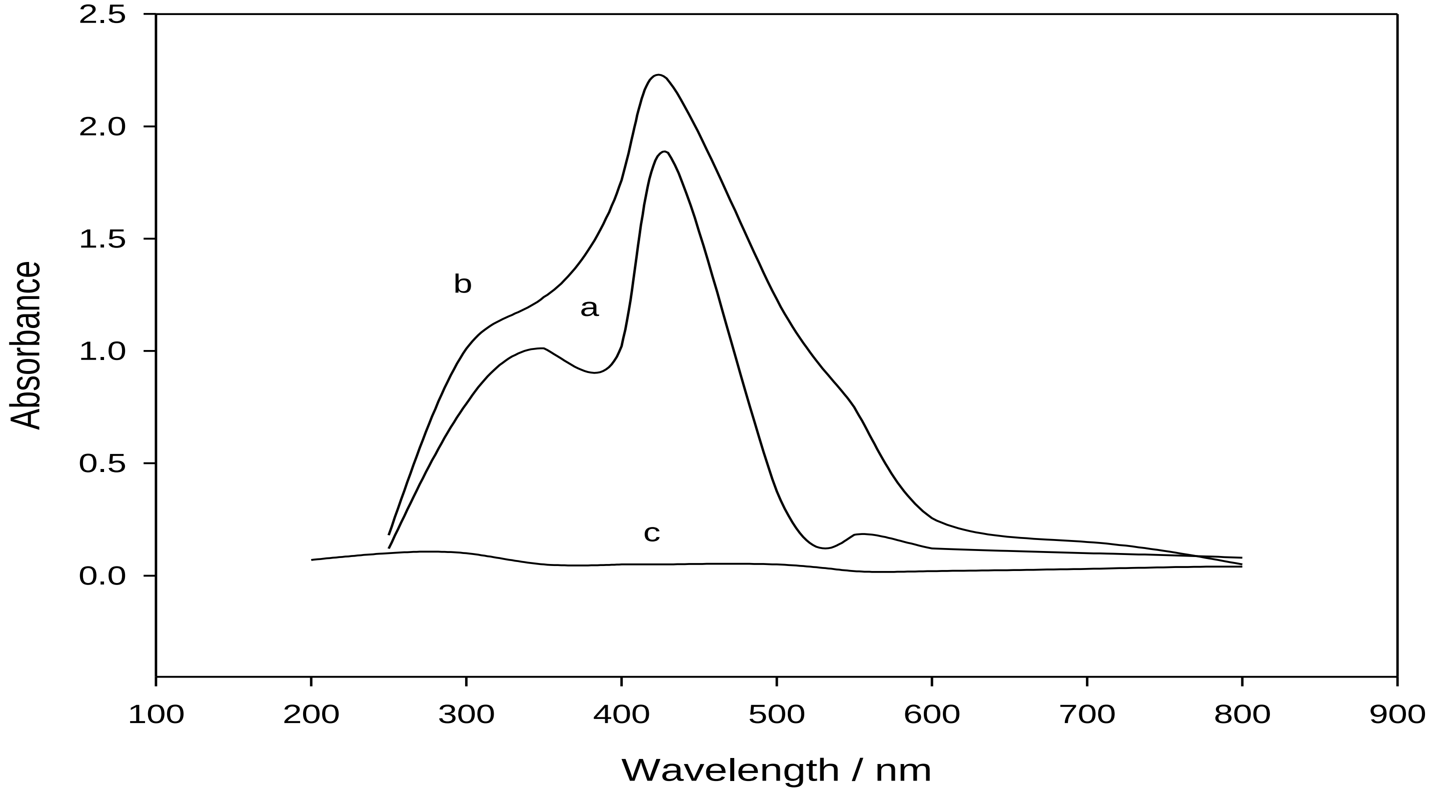


Figure 1. Absorption spectrum of the diazocouple of nitrite with 1,3 dinitrobenzene against reagent blank (a); absorption spectrum of the diazocouple of nitrite with 2,4 dinitrophenyl hydrazine against reagent blank (b) and reagent blank against distilled water (c).

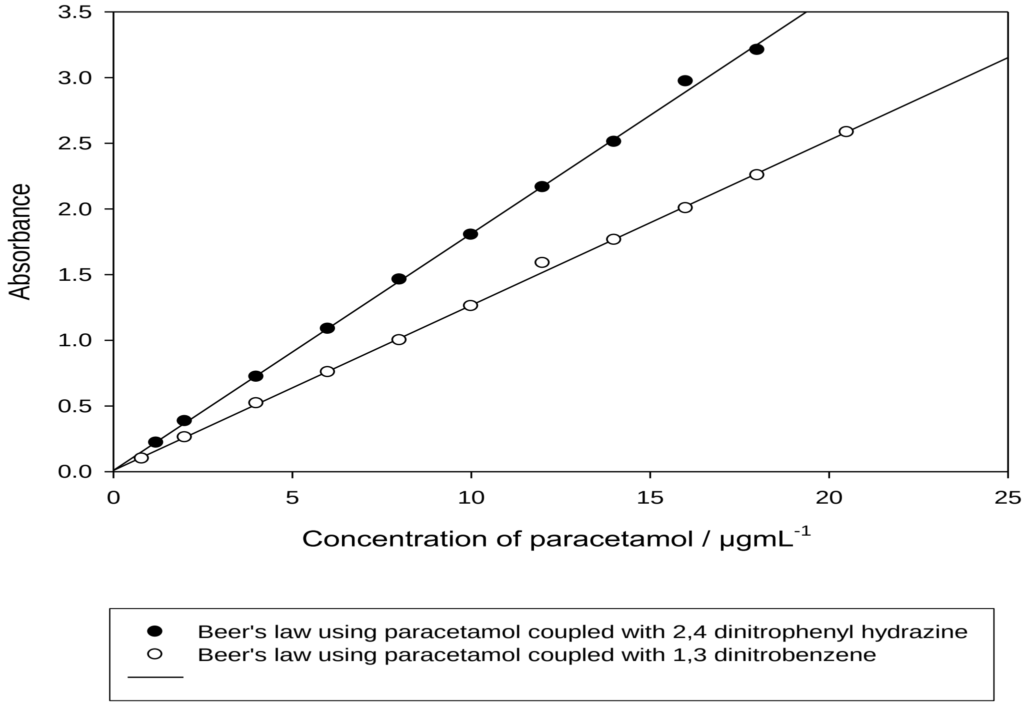
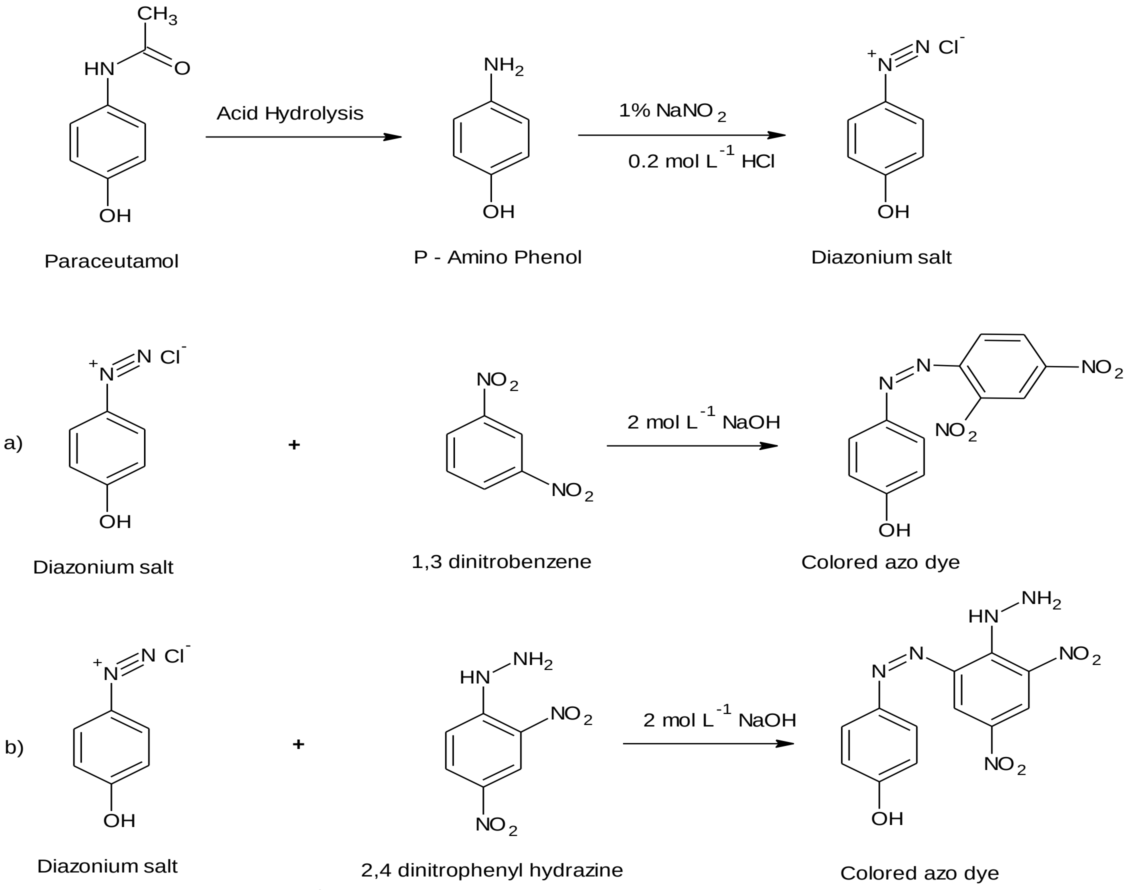


Figure 2. Adherence to Beer's law using 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine as coupling agents.



Scheme 1. Formation of colored azo dye.

3.1 Effect of acid concentration, acids and temperature

The acidity effect on the diazotization reaction was considered with 2 µg mL^{-1} of paracetamol, in the range 0.1- 0.6 mol L^{-1} HCl. From the results, it can be observed that 0.5 mL of 0.5 mol L^{-1} HCl is the suitable concentration which gives the highest value of absorbance, for diazocouple of nitrite with 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine, beyond this range, a decrease in the absorbance was detected (Tab. 1).

Table 1. Effect of acid concentration on absorbance.

0.5 mL HCl used (mol L^{-1})	Absorbance (A)	
	1,3 dinitrobenzene	2,4 dinitrophenyl hydrazine
0.1	0.226	0.202
0.2	0.243	0.215
0.3	0.259	0.236
0.4	0.253	0.238
0.5	0.285	0.242
0.6	0.271	0.234

The effect of the amount of different acid (weak and strong) for the diazotization of paracetamol with nitrite, followed by the coupling of 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine have been investigated. The results indicated that 0.5 mL of 0.5 mol L^{-1} HCl produces the highest intensity for the dye, so it has been selected in the subsequent experiments (Tab. 2). Diazotization was conceded at room temperature (25 ± 5) ^{0}C.

Table 2. Effect of different acid concentration on absorbance.

0.5 mol L^{-1} acid concentration used	Absorbance (A) / mL of acid used			
	0.25 mL	0.5 mL	0.75 mL	1.0 mL
HCl	0.222	0.252	0.244	0.201
HNO_3	0.217	0.243	0.237	0.296
H_2SO_4	0.215	0.222	0.219	0.263
CH_3COOH	0.297	0.217	0.295	0.212

3.2. Effect of the nitrite concentration

The color is reached maximum intensity when using 1 mL of 0.5% sodium nitrite solution using paracetamol-1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine with 2 µg mL^{-1} of paracetamol and adding 1 mL of 0.1-1.0% solutions of the nitrite in hydrochloric acid (0.5 mol L^{-1}) to a series of nitrite solutions. Higher concentration did not build up the absorbance further, and at lower concentration, no good results were obtained.

3.3 Effect of coupling agent

1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine is used as a coupling agent was in the current procedure, by taking 2 µg mL^{-1} of paracetamol and adding 0.25-2.0 mL of 2% 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine to a string of nitrite solutions. It was found that utmost and firm color was obtained with 1 mL of 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine (2%) solution in an ultimate volume of 10 mL.

3.4 Effect of NaOH concentration

The experiment showed that 1.5 mL of NaOH gave utmost absorbance and 1.5 mL of 2 mol L^{-1} NaOH solutions was preferred for the diazotization of paracetamol with nitrite, followed by the coupling of 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine using 2 µg mL^{-1} of paracetamol. Other alkaline solutions were applied, but the finest results were gained by the use of NaOH solution (Tab. 3).

Table 3. Effect of NaOH on absorbance.

2 mol L^{-1} sodium hydroxide used (mL)	Absorbance(A)	
	1,3 dinitrobenzene	2,4 dinitrophenyl hydrazine
0.5	0.218	0.212
1.0	0.224	0.216
1.5	0.257	0.232
2.0	0.243	0.226

3.5 Interference of foreign compounds

The results specified that the studied foreign compounds such as 1000 µg mL^{-1} of glucose, 800 µg mL^{-1} of fructose, 500 µg mL^{-1} of lactose, 500 µg mL^{-1} of starch and 200 µg mL^{-1} of urea do not interfere in the determination of 2 µg mL^{-1} of paracetamol. An error below ±2% error in the absorbance values of paracetamol at 2 µg mL^{-1}.

3.6 Analytical data

By plotting absorbance beside concentration of paracetamol, a straight line is obtained in the graph. Beer's law obeys in the range of 0.8-20.5 μg mL^{-1} of paracetamol with 1,3 dinitrobenzene or 0.5-18.4 μg mL^{-1} of paracetamol with 2,4 dinitrophenyl hydrazine. The molar absorptivity of colored system with nitrite-1,3 dinitrobenzene or nitrite-2,4 dinitrophenyl hydrazine were 1.965×10^{4} L mol^{-1}cm^{-1} or 2.776×10^{4} L mol^{-1}cm^{-1}, and the Sandell's sensitivity of colored system with nitrite-1,3 dinitrobenzene or nitrite-2,4 dinitrophenyl hydrazine were found to be 7.692×10^{-3} μg cm^{-2} or 5.698×10^{-3} μg cm^{-2}.

The detection limit (D_L = 3.3 σ / S) and quantitation limit (Q_L= 10 σ / S) of paracetamol with 1,3 dinitrobenzene or paracetamol with 2,4 dinitrophenyl hydrazine were found to be 0.264 μg mL^{-1} and 0.80 μg mL^{-1} or 0.239 μg mL^{-1} and 0.724 μg mL^{-1} [where σ = Standard Deviation, (n=5) and S = Slope of the curve] and correlation coefficient of paracetamol with 1,3 dinitrobenzene or paracetamol with 2,4 dinitrophenyl hydrazine were 0.9991 or 0.9992.

3.7 Comparison of the current method with other spectrophotometric methods

A comparison of the current method with other spectrophotometric methods are reported for paracetamol determination (Tab. 4). As can be seen, the molar absorptivity, Sandell's sensitivity and color stability (more than 12 h) of the proposed method are comparable or better than other reported methods. The proposed method exhibited excellent selectivity, repeatability, and ease of operation. Thus, the presented method could be of great interest especially for determination of paracetamol in routine analytical laboratories.

Table 4. Comparison of the proposed method with other spectrophotometric methods.

Reagent used	**λ_{max} / nm**	**ε × 10^{4} / L mol^{-1} cm^{-1}**	**Beer's law limits / μg mL^{-1}**	**Sandell's sensitivity / μg cm^{-2}**	**Remarks**	**Ref. No**
8-hydroxyquinoline or 2-naphthol	470 or 490	1.9 or 2.46	2-10	7.9×10^{-3} or 5.9×10^{-3}	---	[10]
1-napthol or resorcinol	505 or 485	1.68 or 2.86	0-10	9.0 ng mL^{-1} cm^{-2} or 5.3 ng mL^{-1} cm^{-2}	Color stability is < than 1 hour	[27]
sodium bismuthate	550 or 560	77.27 or 100.0	100-300 in HCl or 300-800 in CH_3COOH	---	Lack of Sandell's sensitivity	[33]
2,4-dichloroaniline	490	3219.69	4-350	---	Lack of application	[36]
Different solvents	243	---	1-30 mg L^{-1}	---	Less sensitive	[38]
Histidine	430	1.118	10-500 μg mL^{-1}	0.0135	Less selective	[41]
2,7-dihydroxy naphthalene	481	1.058	1-14	0.0142	---	[38]
Proposed method 1, 3 dinitrobenzene or 2, 4 dinitrophenyl hydrazine	429 or 430	1.965 or 2.776	0.8-20.5 or 0.5-18.4	7.692×10^{-3} or 5.698×10^{-3}	---	

3.8 Applications

The current scheme was useful for the determination of paracetamol in pharmaceuticals samples. The relative standard deviation for all five samples ranged from 0.53-1.83% at 95% confidence. The percentage recoveries were found to the range from 98.20 – 100.40. The outcomes were compared with the reference method[36,41] (Tab. 5). The additional ingredients present in pharmaceutical sample appearances did not form hinder.

Table 5. Determination of paracetamol in different pharmaceutical samples using 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine as coupling agent.

Pharmaceutical Samples	**Sample taken / µgmL^{-1}**	**Proposed method**		**Relative Standard Deviation / %**		**Recovery / % of**	
		1,3 dinitrobenzene **Sample found ±SD^{a} / µg mL^{-1}**	2,4 dinitrophenyl hydrazine **Sample found ±SD^{a} / µg mL^{-1}**	1,3 dinitrobenzene	2,4 dinitrophenylhydrazine	1,3 dinitrobenzene	2,4 dinitrophenyl hydrazine
P-750 (750 mg/tab)	5.0 10.0 15.0	5.00 ± 0.04 9.98 ± 0.06 14.96 ±0.08	4.96 ± 0.05 9.94 ± 0.07 14.92 ±0.09	0.80 0.60 0.53	1.00 0.70 0.60	100.00 99.80 99.73	99.20 99.40 99.46
Dolopar (650 mg/tab)	5.0 10.0 15.0	5.01 ± 0.05 9.95 ± 0.08 14.94 ±0.09	5.00 ± 0.08 9.91 ± 0.08 14.90±0.10	0.99 0.80 0.60	1.60 0.81 0.67	100.20 99.50 99.60	100.00 99.10 99.33
Disprin Paracetamol (500 mg/tab)	5.0 10.0 15.0	4.97 ± 0.06 9.97 ± 0.08 14.98 ±0.09	4.92 ± 0.09 9.90± 0.10 14.93±0.10	1.21 0.80 0.60	1.83 1.01 0.67	99.40 99.70 99.87	98.40 98.60 99.53
CrocinQuik (500 mg/tab)	5.0 10.0 15.0	5.01 ± 0.06 9.99 ± 0.09 14.98 ±0.10	4.91 ± 0.07 9.89 ± 0.11 14.92 ±0.12	1.19 0.90 0.67	1.42 1.11 0.80	100.20 99.90 99.86	98.20 98.90 99.46
Paramet (500 mg/tab)	5.0 10.0 15.0	4.99 ± 0.08 10.00± 0.08 14.96 ±0.09	4.94 ± 0.04 9.88± 0.07 14.87 ±0.10	1.60 0.80 0.60	0.81 0.71 0.67	99.80 100.00 99.73	98.80 98.80 99.13
Nicetamol (125 mg/tab)	5.0 10.0 15.0	5.02 ± 0.08 9.92± 0.08 14.99±0.09	4.97 ± 0.08 9.96 ± 0.09 14.83±0.09	1.59 0.81 0.60	1.61 0.90 0.61	100.40 99.20 99.93	99.40 99.60 98.87
Paracip (500 mg/tab)	5.0 10.0 15.0	4.97 ± 0.06 9.94± 0.08 14.94±0.10	4.93 ± 0.09 9.83± 0.06 14.85±0.09	1.21 0.80 0.66	1.82 0.61 0.60	99.40 99.40 99.60	98.60 98.30 99.00

a. Mean (n=5) ± SD {standard deviation}.

4. Conclusions

This study demonstrated that spectrophotometric analysis is a very powerful methodology for the determination of paracetamol. For the first time 1,3 dinitrobenzene or 2,4 dinitrophenyl hydrazine is used as coupling agent for the determination of paracetamol in pharmaceutical dosage samples using an easy and simple spectrophotometric method. The proposed method has an ample range of applications with no need of heating, cooling, extraction and has high color stability (12 h). The percentage recoveries were found in the range from 98.20 – 100.40 which complete the legitimacy of the method for the analysis of paracetamol in pharmaceutical formulations. Moreover, the current method is more effective than the methods reported in the literature and has been effectively applied to the spectrophotometric analysis of determination of paracetamol in several pharmaceutical dosage samples.

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Major and minor head losses in a hydraulic flow circuit: experimental measurements and a Moody's diagram application

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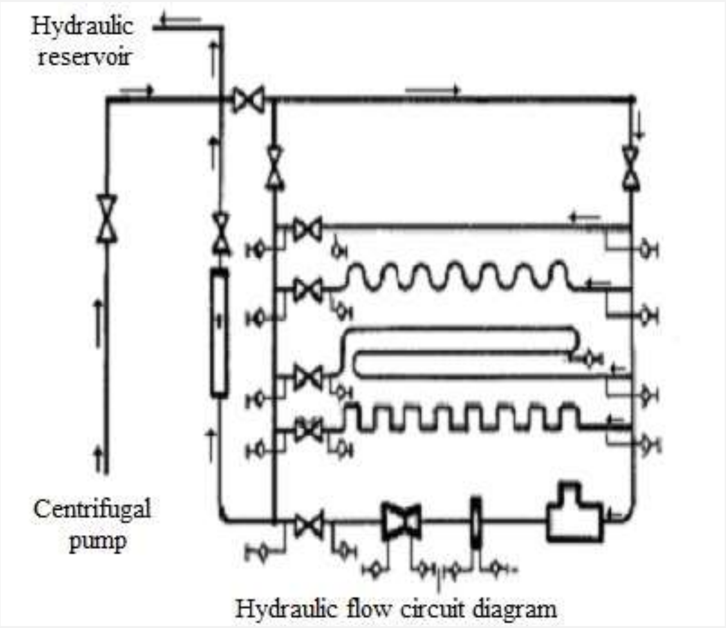
ABSTRACT: Domestic and industrial hydraulic drainage networks have gradually become more complicated because of the cities' rapid expansion. In surcharged hydraulic systems, the head losses may become rather significant, and should not be neglected because could result in several problems. This work presents an investigation about major and minor head losses in a hydraulic flow circuit, simulating the water transport in a drainage network at room temperature (298.15 K) under atmospheric pressure (101,325 Pa). The losses produced by the fluid viscous effect through the one used cast-iron rectilinear pipe (RP-11) and the localized losses generated by two flow appurtenances, one fully open ball valve (BV-1) and one module of forty-four 90º elbows (90E-8) were experimentally measured. Experimental data generated head-loss curves and their well fitted to potential regressions, displaying correlation coefficients (R^2) of 0.9792, 0.9924, and 0.9820 for BV-1, 90E-8, and RP-11, respectively. Head loss experimental equations and local loss coefficients through BV-1 and 90E-8 were determined successfully. The Moody's diagram application proved to be a quite appropriate tool for an approximate estimation of Darcy-Weisbach friction factor. A good approximation between friction factor values obtained via experimental measurements and the Moody's diagram was observed with mean absolute deviate of 0.0136.



1. Introduction

Pipeline systems range from the quite simple ones to large and quite complex ones. They may be as uncomplicated as a single pipe conveying water from one reservoir to another or they may be as elaborate as an interconnected set of water distribution networks for a major metropolitan area[1]. The hydraulic drainage domestic and industrial networks have gradually become more complicated and diverse because of the cities' rapid urbanization and expansion. In surcharged hydraulic systems, the head losses may become rather significant, and should not be neglected because could result in several problems, such as inappropriate drainage pipes, insufficient carrying capacities, blowout of manhole covers and the occurrence of floods, for example[2].

Groundwater flow and solute transport in fractured rock is of great interest in nuclear waste disposal, contaminant control, and oil recovery. The friction factor is an important parameter in identifying the characteristics of flow and solute hydraulic transport. During the last several decades, several theoretical and experimental researches have been conducted to investigate the relationship between the friction factor and the Reynolds number. Colebrook[3] realized experiments on several types of pipes and the results were correlated to the well-known Colebrook equation. Later, Moody[4] presented Colebrook's results in a graphical format, which is called the Moody diagram[5,6]. Moody's diagram represents the plots of the Colebrook equation over a very wide range of the Reynolds number (Re from 2320 to 10^8) and relative roughness values (ε/D from 0 to 0.05)[7].

According to LaViolette[8], Moody's chart provides an easy and accurate way of solving hydraulic flow and dimensioning problems, making it an extremely useful tool and unmistakable simplicity adopted by engineers to understand the behavior of viscous flows and evaluate the loss of energy due to viscous friction. The diagram is available in most fluid mechanics textbooks and is widely used to estimate the effects of pipe roughness on pipe friction as a function of Reynolds number[9].

Water flows are turbulent flows and the hydraulic calculations in water networks still have certain indetermination, particularly due to the velocity of the flow is rather small[10,11]. In a typical system with long pipes, there are the major head losses, related to friction between the flowing fluid and pipeline systems, and minor losses. Although this is generally true, in some cases the minor losses may be greater than the major losses. This is the case, for example, in systems with several turns and valves in a short distance. Several design parameters of pipelines used in domestic and industrial networks could be calculated and optimized if all major and minor head losses of such pipelines are well estimated by hydraulic calculations[10].

Local head losses are any energy loss caused by some localized disruption of the flow due to the presence of various flow appurtenances, such as valves, bends, elbows, inlets, exits, enlargement, and contractions in addition to the pipes. These components interrupt the smooth flow of the fluid and cause additional losses because of the flow separation and mixing they induce. If a loss is sufficiently small in comparison with other energy losses and with pipe friction, it may be regarded as a minor loss. Often minor losses are neglected, or they are known to be quite small, as happen in very long pipes. However, some local losses can be so large or significant that they will never be termed a minor loss. Normally, theory alone is unable to quantify the magnitudes of the energy losses caused by these devices, so the representation of these losses depends heavily upon experimental data[1].

In this context, the present work ambulates to delineate a new investigation about major and minor head losses in a hydraulic flow circuit used for water fluid transport at room temperature (298.15 K) under atmospheric pressure (101,325 Pa). It strives to measure the head losses produced by the fluid viscous effect through the rectilinear pipe of used cast-iron and the localized losses generated by one fully open ball valve and one module composed by forty-four 90º elbows. Focusing on the experimental determinations of the local head loss coefficients and of the Darcy-Weisbach friction factor, besides providing subsidies for an application of Moody's diagram to the behavior of the hydraulic flow of the mentioned circuit. In addition, this work aims at presenting an application approach of theoretical concepts associated with fluid mechanics' and hydraulic's intrinsic fundamentals in the understanding of how head loss measurements can to aid to develop improvements and solutions in the scope of surcharged hydraulic systems of drainage networks.

2. Experimental

Experimental measurements of major and minor head losses were realized in hydraulic flow circuit at room temperature (298.15 K) under atmospheric pressure (101,325 Pa) using water as fluid flow, based on the methodology proposed by Buonicontro[12]. The circuit was composed by a test bench with a pressure-loss module (Didacta, model SUE 14D SU) containing one ball valve, one module of forty-four 90º elbows, and one rectilinear pipe of used cast-iron (Figs. 1 and 2).

In the first test, measures of variability in volumetric flow rate (m^3 h^{-1}) and the corresponding pressure loss (mmHg) were experimentally collected through of the fully open ball valve (BV-1) (Fig. 3). For that, only the connections between the BV-1 and differential pressure gauge (DPG-19) (Fig. 4) were kept open, so that, the components: male-female valve (MFV-2); diaphragm valves (DV-3 and DV-14); drawer valves (DV-4 and DV-16); butterfly valve (BV-5) were closed and the components: ball valve (BV-1); drawer valves (DV-15, DV-17, and

DV-18) were opened. Then, the hydraulic circuit centrifugal pump was started and DV-14 was slowly open for flow and pressure variation readings, using rotameter (R-13) (Fig. 5) and differential pressure gauge (DPG-19), respectively. Readings were realized in hydraulic flow range of 3.0 to 9.0 $m^3 h^{-1}$. Figure 6 presents the identification of all hydraulic circuit components and Tab. 1 exhibits the ball valve's experimentally measured data.

Figure 1. Hydraulic flow circuit.

Figure 2. Hydraulic flow circuit control panel.

Figure 3. Ball valve.

Figure 4. Differential pressure gauge coupled to the circuit.

Figure 5. Rotameter coupled to the circuit.

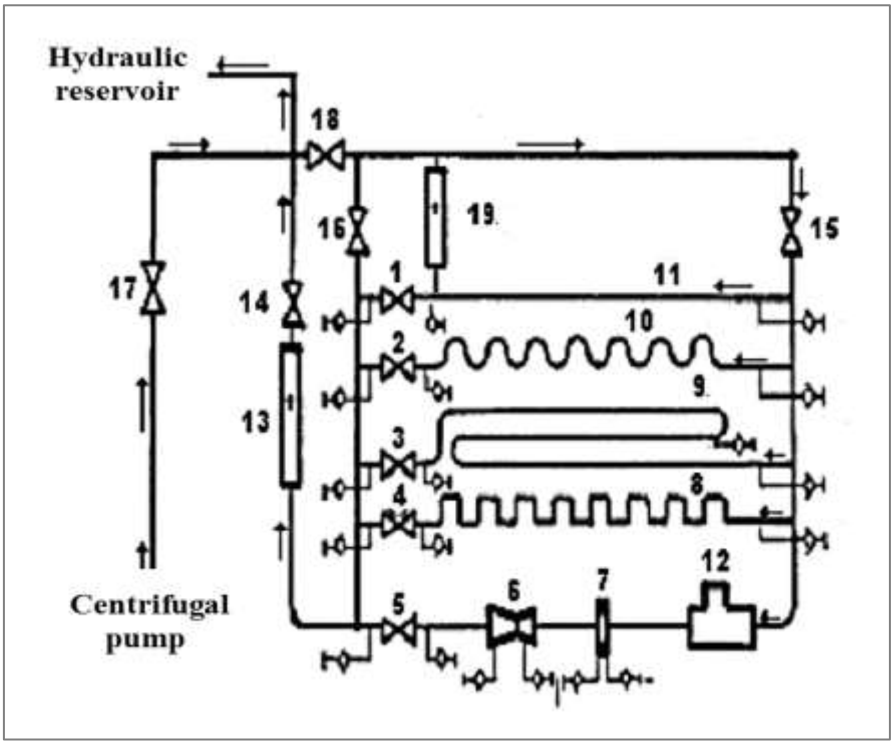


Figure 6. Hydraulic flow circuit identification diagram (BV-1: ball valve; MFV-2: male-female valve; DV-3 and DV-14: diaphragm valves; DV-4, DV-15, DV-16, DV-17, and DV-18: drawer valves; BV-5: butterfly valve; VM-6: venturi meter; OPM-7: orifice plate meter; 90E-8: module of forty-four 90º elbows; RP90C-9: rectilinear pipe with 90º curve; 90C-10: 90º curves module; RP-11: rectilinear pipe; H-12: hydrometer; R-13: rotameter; DPG-19: differential pressure gauge).

Table 1. Ball valve experimental data.

Flow / $m^3\ h^{-1}$	Flow / $m^3\ s^{-1}$	Head Loss / mmHg	Head Loss / mH_2O	Experimental Constant / $mH_2O\ (m^3\ s^{-1})^{-2}$	Mean Experimental Constant / $mH_2O\ (m^3\ s^{-1})^{-2}$	Statistical Parameters (Values in Module)		
						Absolute Deviate	Relative Deviate	Percentage Deviation/%
3.0	8.3E-04	1.0	1.4E-02	2.0E+04	3.3E+04	1.3E+04	4.1E-01	40.8
4.0	1.1E-03	3.0	4.1E-02	3.3E+04		2.3E+01	7.0E-04	0.1
5.0	1.4E-03	5.0	6.8E-02	3.5E+04		2.2E+03	6.6E-02	6.6
6.0	1.7E-03	7.0	9.5E-02	3.4E+04		1.2E+03	3.6E-02	3.6
7.0	1.9E-03	10.0	1.4E-01	3.6E+04		2.9E+03	8.8E-02	8.8
8.0	2.2E-03	14.0	1.9E-01	3.9E+04		5.5E+03	1.7E-01	16.6

In the second test, measures of variability in volumetric flow rate (m^3 h^{-1}) and the corresponding pressure loss (mmHg) were gathered through of the module of forty-four 90º elbows (90E-8). For this, the connection valves of flow input of the first elbow and flow output of the last elbow with the DPG-19 were opened, so that, the components BV-1, MFV-2, DV-3, DV-14, BV-5, and DV-16 were closed and the components DV-4, DV-15, DV-17, and DV-18 were opened. Next, the centrifugal pump was started, and DV-14 was slowly open for flow and pressure variation readings, using R-13 and DPG-19, respectively. Readings were realized in hydraulic flow range of 3.0 to 6.0 m^3 h^{-1}. Table 2 exhibits the 90º elbows module obtained data.

Finally, in the third test, measures of variability in volumetric flow rate (m^3 h^{-1}) and the pressure loss (mmHg) were collected through of the rectilinear pipe of used cast-iron (RP-11) of length of 2.2 m and diameter of 0.0365 m. For that, the connections between the RP-11 and DPG-19 were kept open, so that, the components MFV-2, DV-3, DV-14, DV-4, DV-16, and BV-5 were closed and the components BV-1, DV-15, DV-17, and DV-18 were opened. Then, the centrifugal pump was started, and DV-14 was slowly open for flow and pressure variation readings, using R-13 and DPG-19, respectively. Readings were realized in hydraulic flow range of 3.0 to 9.0 m^3 h^{-1}. Table 3 shows the rectilinear pipe obtained data.

Table 2. 90º elbows module experimental data.

Flow / m^3 h^{-1}	Flow / m^3 s^{-1}	Total Head Loss / mmHg	Unit Head Loss / mmHg	Unit Head Loss / mH_2O	Experimental Constant / mH_2O $(m^3$ $s^{-1})^{-2}$	Mean Experimental Constant / mH_2O $(m^3$ $s^{-1})^{-2}$	Statistical Parameters (Values in Module)		
							Absolute Deviate	Relative Deviate	Percentage Deviation/%
3.0	8.3E-04	110.0	2.5E+00	3.4E-02	4.9E+04	5.4E+04	4.6E+03	9.1E-01	91.4
3.5	9.7E-04	144.0	3.3E+00	4.5E-02	4.7E+04		6.5E+03	8.8E-01	87.9
4.0	1.1E-03	206.0	4.7E+00	6.4E-02	5.2E+04		2.0E+03	9.6E-01	96.3
4.5	1.3E-03	295.0	6.7E+00	9.1E-02	5.8E+04		4.8E+03	1.1E+00	109.0
5.0	1.4E-03	358.0	8.1E+00	1.1E-01	5.7E+04		3.8E+03	1.1E+00	107.1
5.5	1.5E-03	422.0	9.6E+00	1.3E-01	5.6E+04		2.3E+03	1.0E+00	104.4
6.0	1.7E-03	500.0	1.1E+01	1.5E-01	5.6E+04		2.1E+03	1.0E+00	103.9

Table 3. Rectilinear pipe data.

Experimental Data						Moody Chart Data			Statistical Parameters (Values in Module)		
Flow / m^3 h^{-1}	Flow / m^3 s^{-1}	Head Loss / mmHg	Head Loss / mH_2O	Unit Head Loss / mH_2O m^{-1}	Friction Factor	Flow Velocity / m s^{-1}	Reynolds Number	Friction Factor	Absolute Deviate	Relative Deviate	Percentage Deviation/%
3.0	8.3E-04	4.0	5.4E-02	2.5E-02	2.8E-02	8.0E-01	2.9E+04	3.6E-02	8.1E-03	3.5E+00	345.4
4.0	1.1E-03	5.0	6.8E-02	3.1E-02	2.0E-02	1.1E+00	3.9E+04	3.5E-02	1.5E-02	1.3E+00	127.7
5.0	1.4E-03	8.0	1.1E-01	4.9E-02	2.0E-02	1.3E+00	4.8E+04	3.5E-02	1.4E-02	1.4E+00	139.6
6.0	1.7E-03	11.0	1.5E-01	6.8E-02	1.9E-02	1.6E+00	5.8E+04	3.4E-02	1.5E-02	1.3E+00	127.9
7.0	1.9E-03	16.0	2.2E-01	9.9E-02	2.1E-02	1.9E+00	6.8E+04	3.4E-02	1.4E-02	1.5E+00	152.1
8.0	2.2E-03	20.0	2.7E-01	1.2E-01	2.0E-02	2.1E+00	7.8E+04	3.4E-02	1.4E-02	1.4E+00	136.6
9.0	2.5E-03	25.0	3.4E-01	1.5E-01	1.9E-02	2.4E+00	8.7E+04	3.4E-02	1.5E-02	1.3E+00	132.7

Equation 1 was used in the calculations of the algebraic determination of the local head loss coefficients of the fully open ball valve and of the module of forty-four 90º elbows. In the determination of the friction factor value of rectilinear pipe were used the Eqs. 2 and 3, derived from the Darcy-Weisbach equation (Eq. 4). Parallelly, the friction factor also was estimated by Moody's diagram (Fig. 7). For this, it was used the relative roughness value (ε/D) of 0.0071, obtained of cast iron roughness (ε = 0.26)[2] and the Reynolds numbers correspondents to each volumetric flow rate were calculated considering the kinematic viscosity of water of 1.0E-06 m^2 s^{-1}, pipe diameter of 0.0365 m, and using Eq. 5. Besides that, statistical parameters – arithmetic mean (M, Eq. 6); absolute deviate (AD, Eq. 7); relative deviate (RD, Eq. 8); percentage deviation (PD, Eq. 9); and mean absolute deviate (MAD, Eq. 10) – were applied to the experimentally obtained data in tests 1, 2, and 3. All results were presented in Tabs. 1, 2, and 3.

$$K_1 = \frac{\Delta H}{Q^2} \tag{1}$$

where: K_1 = constant relative to flow and pressure variation readings [mH_2O $(m^3$ $s^{-1})^{-2}$]; ΔH_L = head loss variation [mH_2O]; Q = flow [m^3 s^{-1}].

$$J = \frac{\Delta H}{L} \tag{2}$$

where: J = unit head loss [mH_2O m^{-1}]; ΔH = head loss variation [mH_2O]; L = length of pipe [m].

$$f = \frac{J}{\frac{8}{\pi^2 D^5 g} Q^2} \tag{3}$$

where: f = friction factor [unitless]; J = unit head loss [mH_2O m^{-1}]; D = diameter of pipe [m]; g = gravitational acceleration [9.81 m^3 s^{-2}]; Q = flow [m^3 s^{-1}].

$$\Delta H = f \frac{L}{D} \frac{V^2}{2g} \tag{4}$$

where: ΔH = head loss variation [mH_2O]; f = friction factor [unitless]; L = length of pipe [m];

D = pipe diameter [m]; V = flow velocity [m s^{-1}]; g = gravitational acceleration [9.81 m s^{-2}].

$$Re = \frac{VD}{\nu} \tag{5}$$

where: Re = Reynolds number [unitless]; V = average velocity of flow [m s^{-1}]; D = diameter of pipe [m]; ν = kinematic viscosity of fluid [m^2 s^{-1}].

$$M = \frac{m_1 + m_2 + m_3 + \ldots + m_n}{n} \tag{6}$$

where: M = arithmetic mean; m_1, m_2, m_3, m_n = measures; n = measures number.

$$AD = measure - M \tag{7}$$

where: AD = absolute deviate; M = arithmetic mean.

$$RD = {}^{AD}/_{M} \tag{8}$$

where: RD = relative deviate; AD = absolute deviate; M = arithmetic mean.

$$PD = |\, RD\ x\ 100\ |\% \tag{9}$$

where: PD = percentage deviation; RD relative deviate.

$$MAD = \frac{AD_1 + AD_2 + AD_3 + \ldots + AD_n}{n} \tag{10}$$

where: MAD = mean absolute deviate; AD_1, AD_2, AD_3, AD_n = AD_1, AD_2, AD_3, AD_n = absolute deviates; n = measures number.

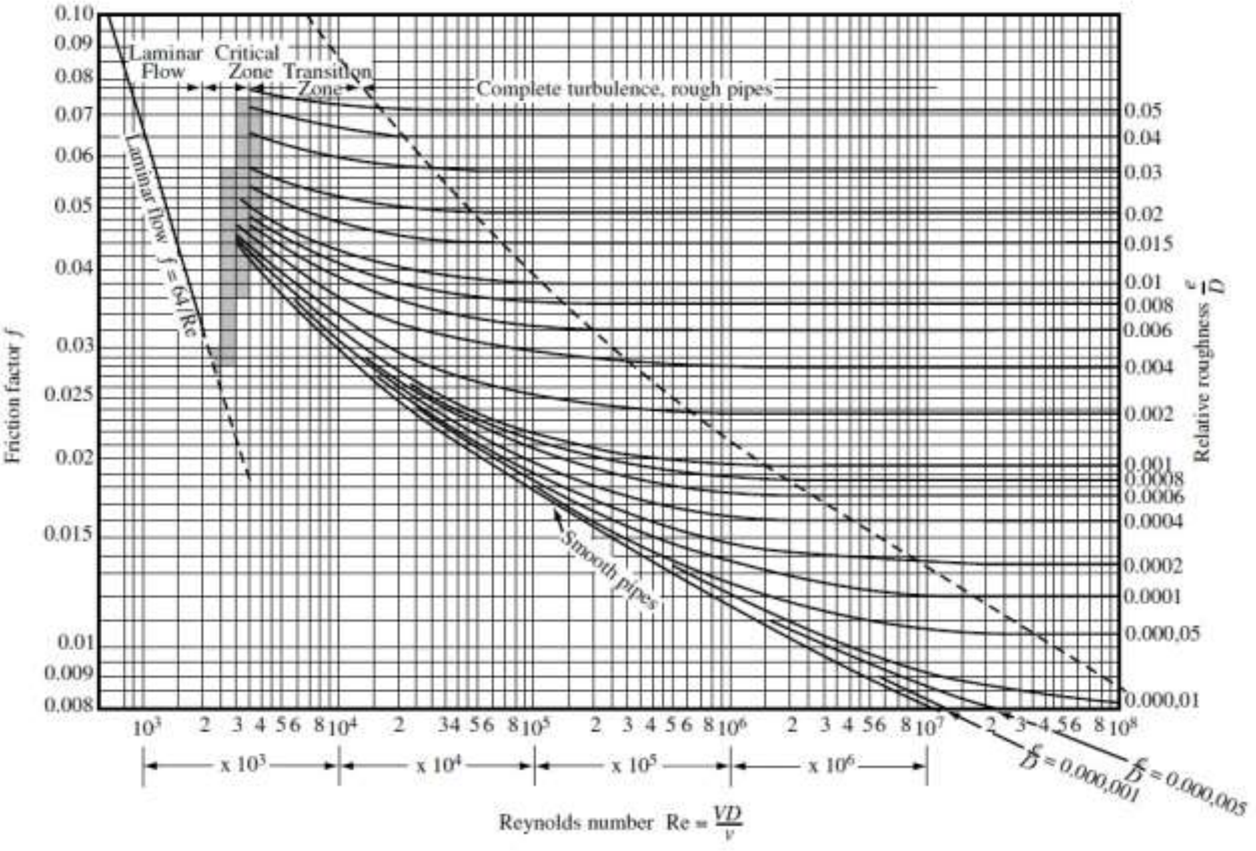


Figure 7. The Moody diagram for the Darcy-Weisbach friction factor.
Source: Larock, Jeppson & Watters[1].

3. Results and Discussion

Major and minor head losses were satisfactorily investigated via experimental measurements in the studied hydraulic flow circuit. Figures 8, 9, and 10 exhibit the curves of head loss versus volumetric flow rate for BV-1, 90E-8, and RP-11, respectively. As can be seen, a parabolic profile was presented by both hydraulic circuit's components, corroborating the proportionality relationship between the frictional and minor losses, and the flow velocity, foreseen by the Darcy-Weisbach equation. So, since flow velocity is directly proportional to the volumetric flow rate, the system head loss must be directly proportional to the square of the volumetric flow rate. Table 4 shows the potential regressions fitted to experimental data with its correspondent correlation coefficients (R^2), as well the head loss experimental equations of aforementioned components.

For purposes of determining the head loss coefficients through BV-1 and 90E-8, the localized head loss equation was written as a function of the volumetric flow rate (Eq. 11)[12]. The algebraic determination of the loss coefficients was given by the ratio between the constant relative to measurements of variability in flow rate and the corresponding pressure loss (K_1) and the constant relative to installation data (k_I). Table 5 lists the recorded results for localized head losses coefficients. The attained difference between the theoretical and experimental values was associated with readings' fluctuations, arising from the unstable operating conditions that always occur in closed-loop pump systems due to pressure pulsation. Beyond the fluctuations related to the centrifugal pump's adjusting to each degree of opening of the control valve in the changing the volumetric flow rate of the fluid[12].

$$\Delta H_L = K_L \frac{V^2}{2g} \overset{V=\frac{4Q}{\pi D^2}}{\therefore} \Delta H_L = K_L \left(\frac{16}{\pi^2 D^4 2g}\right) Q^2 \overset{k_I=\left(\frac{8}{\pi^2 D^4 g}\right)Q^2}{\therefore} \Delta H_L = K_L k_I Q^2 \therefore \Delta H_L = K_1 Q^2 \tag{11}$$

where: ΔH_L = localized head loss variation [mH_2O]; K_L = local head loss coefficient; V = flow velocity [$m\ s^{-1}$]; Q = flow [$m^3\ s^{-1}$]; D = pipe diameter [m]; g = gravitational acceleration [$9.81\ m\ s^{-2}$]; k_I = constant relative to installation data; K_1 = constant relative to flow and pressure variation readings.

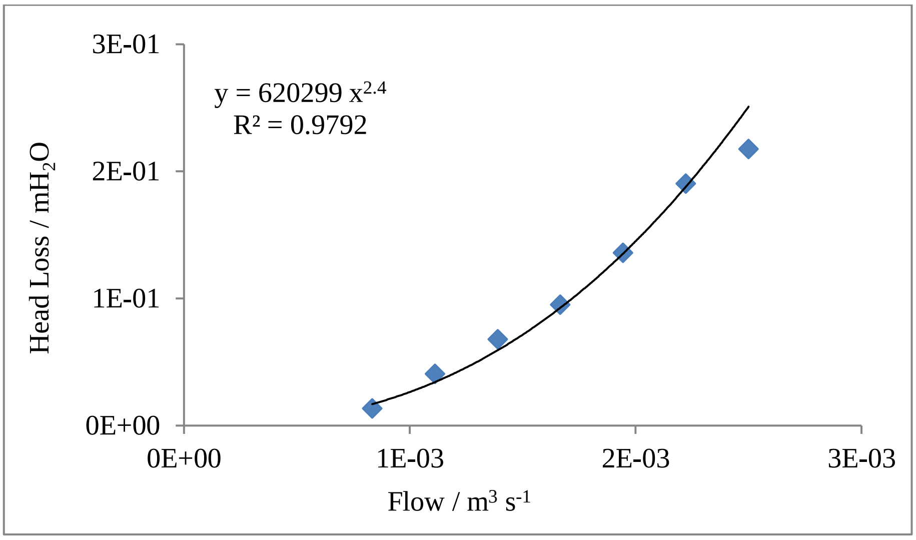


Figure 8. Head loss curve for the ball valve.

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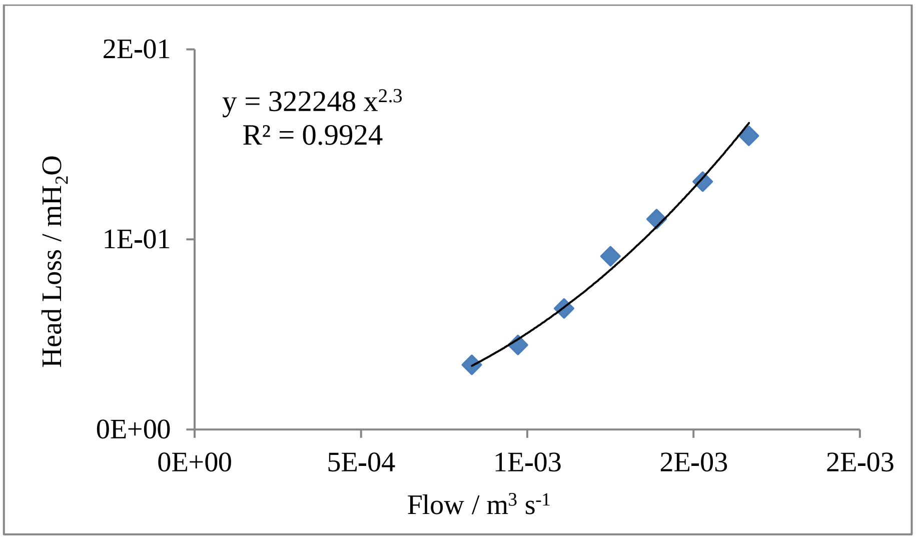

Figure 9. Head loss curve for the 90º elbow.

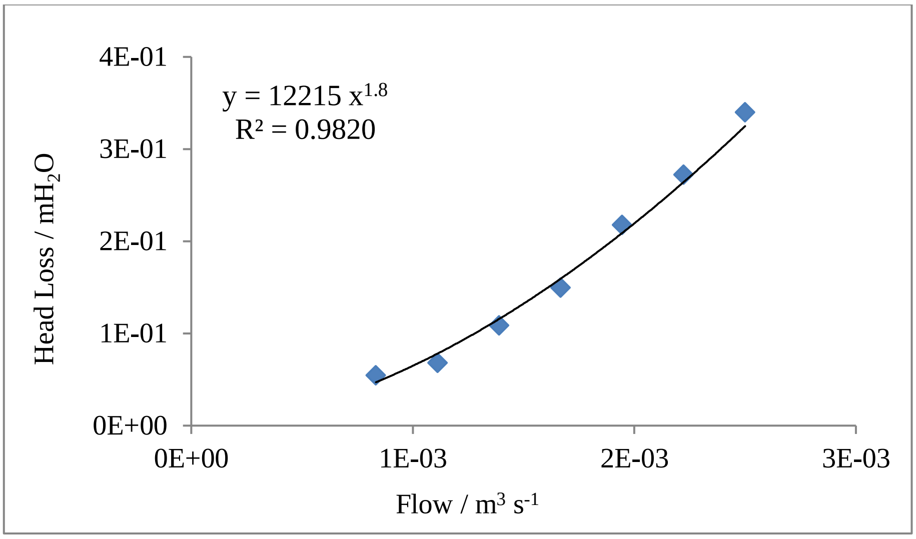

Figure 10. Head loss curve for the rectilinear pipe.

Table 4. Hydraulic circuit components parameters and equations determined from experimental data.

Hydraulic Circuit Component	Head Loss Experimental Equation	Potential Regression	Correlation Coefficient (R^2)
BV-1	$\Delta H = 33000\, Q^2$	$y = 620299\, x^{2.4}$	0.9792
90E-8	$\Delta H = 54000\, Q^2$	$y = \ 322248\, x^{2.3}$	0.9924
RP-11	–	$y = \ 12215\, x^{1.8}$	0.9820

Table 5. Constants and coefficients of localized head losses through ball valve and 90º elbows module.

Hydraulic Circuit Component	Experimental Data Constant / $mH_2O\ (m^3\ s^{-1})^{-2}$	Constant Relative to Installation Data	Head Loss Theoretical Coefficient[1]	Head Loss Experimental Coefficient
BV-1	3.3E+04	4.655E+04	7.00E+10	7.10E–01
90E-8	5.4E+04		9.00E–01	1.15E+00

Friction factor value of rectilinear pipe of used cast-iron (RP-11) was satisfactorily determined by the application of the Darcy-Weisbach equation (Eq. 2)[12] to the experimental data. Similarly, the Moody diagram application proved to be a quite appropriate tool to evaluate the effects of relative roughness (0.0071) on a function of Reynolds number (29069 to 87208) in friction factor estimates. The recorded factors via chart were obtained in the turbulent transition zone, in which the Colebrook-White equation (Eq. 12)[12] can be used to replicate numerically the experimental data, located below of region of complete turbulence for rough pipes and above of region of smooth turbulence. By comparing the factors obtained via experimental measurements and via diagram, a good approximation between the values was observed, with mean absolute deviation of 0.0136.

$$\frac{1}{\sqrt{f}} = 1.14 - \left(2\, log_{10} \frac{\varepsilon}{D}\right) + \left(\frac{9.35}{Re\sqrt{f}}\right) \qquad (12)$$

where: f = friction factor [unitless]; ε = pipe roughness [mm]; D = pipe diameter [mm]; Re = Reynolds number [unitless].

Fluid mechanic's fundamentals to the internal turbulent flow of water as fluid flow in a hydraulic circuit were rightly applied. Normal head losses produced by fluid viscous effects and the localized losses depending on the geometry singularities of the pipe were successfully determined. Viscous effects on flow and head losses associated with the piping design were discussed. Characteristics such as the pipe roughness, as well as velocity and viscosity of the fluid were used as parameters for algebraic determination of the friction factor value associated with the circuit's rectilinear pipe. Experimental coefficients of localized losses through ball valve and 90° elbows module were measured and compared with its respective theoretical values.

This work showed how simple measures of volumetric flow rate and the pressure variation may be useful to measure major and minor head losses in hydraulic drainage networks and how Moody's diagram can be applied to understand the behavior of viscous flows and evaluate the loss of energy due to viscous friction. Furthermore, the results provided could be useful to solve flow problems in surcharged hydraulic systems where the head losses cannot be neglected or for dimensioning and optimization studies of design parameters of drainage networks of groundwater flow and hydraulic transport. So, hydraulic calculations estimates can help avoid several problems, such as inappropriate drainage pipes, insufficient carrying capacities, and the occurrence of floods, already that the theory alone is unable entirely to quantify the magnitudes of the energy hydraulic losses.

4. Conclusions

Measurements of variability in volumetric flow rate and the corresponding pressure loss, as well Moody's diagram application allowed to investigate major and minor head losses associated water flow in the studied hydraulic circuit, suggesting the suitability of the proposed methodology. Experimental data generated curves of head loss and their well fitted to potential regressions, displaying correlation coefficients (R^2) of 0.9792, 0.9924, and 0.9820 for ball valve, 90° elbows module, and rectilinear pipe, respectively. Head loss experimental equations and local loss coefficients through ball valve and 90° elbows module were determined successfully. The Moody's diagram application proved to be a quite appropriate tool for an approximate estimation and with reasonable accuracy of friction factor value of rectilinear pipe of used cast-iron. A good approximation between factors values obtained via experimental measurements and the diagram was observed with mean absolute deviate of 0.0136.

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A comprehensive review of database resources in chemistry

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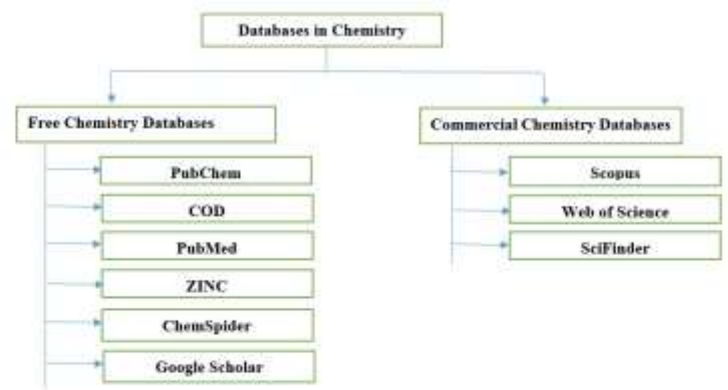
ABSTRACT: As scientific community worldwide is publishing a huge number of research articles in various fields; it is necessary to distinguish between databases that are efficient and objective for literature searches. This review offers information on the important points of the database. None of the databases are complete and perfect, but they complement each other. If a library can only afford one, choice must be based on the priorities of institutional needs. The benefits that databases can provide in the preparation of the literature review for developing future studies and dissemination of research are discussed. This paper provides an overview of the most frequently used free chemistry databases such as PubChem, Crystallography Open Database, PubMed, ZINC, ChemSpider, and Google Scholar. It also gives a brief description of three major commercial databases such as Scopus, Web of Science, and SciFinder. Thus, substance and citation databases that covers almost all areas of chemistry, has become an invaluable tool in bibliometric analysis.



1. Introduction

The amount of information available today is growing at an exponential rate and the ability to search for the necessary information is one of the basic needs of knowledge. The abundance of technological and Internet resources can both simplify and complicate a researcher's world. Chemistry is an interdisciplinary subject upon which the other scientific disciplines are dependent to a certain extent. This vast information data must be systematically organized by the experts in the field. A database is an organized collection of data in any field[1]. In addition to the basic search techniques that are used today in almost everyday life, such as searching by keyword search engines, there are some areas of chemistry that are not so simple or meaningful. Chemical databases have now become a powerful tool in drug discovery. Database searches based on potential requirements for biological activity identifies compounds that are suitable for detailed analysis or indicate novel ways to achieve the desired activity[2]. Accessing chemical information that are stored in different kinds of databases by utilizing the means of computer are gradually becoming more significant. The dimension of all databases either in terms of the structures or that of the reactions are growing tremendously each year[3]. The proficiency of search algorithms executed within these databases are very crucial. Therefore, the computer supported databases are becoming useful tools for several research laboratories in industry as well as in academia.

It is must to have a better understanding of how the data is organized and interconnected for the effective search in any database. The databases are broadly distributed in two major group's viz. full-text and the structures, based on the category of data contained[4]. A full-text database is generally a set of documents in which indexes are created to facilitate their fast search. This type of database is commonly run by publishers of magazines and books, patent offices for patents or academic institutions. The largest database of this type on this globe is definitely operated by Google, in which documents and other accessible files are uploaded on the internet in the form of websites[5]. On the other hand, structured databases normally include a set of tables that contain records or rows, all of which have the same structure well defined by a set of fields or columns[6]. Each record is always assigned a unique "ID" or "Number" called as identifier or the primary keys, which are easily referenced. The Chemical Abstracts Service Registry Number (CAS RN) is an example of the primary key for the structure in the REGISTRY database[7]. Structured databases are generally classified into two large groups in terms of its contents as bibliographic and factographic. The bibliographic databases usually do not have the full text of a document, however it records information about a single publication, patents, and similar documents[8]. Typical fields in bibliographic records are - author, article title, journal name, volume, issue, year of publishing, pages, etc. The Digital Object Identifier (DOI) is a comparatively new parameter, which describes the distinctive placement of a document on the Web[9]. The bibliographic databases are secondary sources that interpret, analyze, and summarize, the primary source information to increase usability and speed of delivery, such as an online encyclopedia. Moreover, factographic databases consist of specific information extracted from primary documents, particularly in the area of chemistry that have details about chemical reactions and chemical compounds such as toxicological, spectral, physical, or chemical characterization[10]. It is must for the databases to allow the user to search for records by all field values as well as to create search queries for logical operators in order to be regarded as an ideal database system. Additionally, the thorough knowledge of the database structure, the syntax of the search language, and specific IT skills are the prerequisite for this search method. The method that is frequently adopted by the database creators is the inclusion of the "forms" which is already having names of the usual fields such as "bibliographic data" or "physical parameters" to give a user-friendly interface.

Search by chemical identifier is probably the simplest search by keyword, with the difference that chemical identifiers are a little more difficult to define. However, the free programs available to us can generate these identifiers if we are able to enter the structure of the compound (e.g. Chem-Sketch or Marvin- Sketch)[11]. The most common search for information on chemical compounds or their chemical products is the search for structures or substructures. Less common were also searched in structured databases under chemical, physical, or biological properties of the chemical compounds. There are many considerations that are involved in the construction and searching of chemical databases. Chemical structures that are commonly stored in databases, such as text, differ significantly from other entities therefore the different search modes too differ significantly, however some matches can be drawn. The reason for the existence of different databases is that each of them have its own function, however, none of them is perfectly a subset of any other. The subsequent process for any chemical databases using a specialized structural editor is to create a search query, give a chemical structure or substructure of a search compound. JME Editor was the most widely used structural editor of this kind but for the last couple of years or more have started to phase out this technology[12]. Consequently, the creators of chemical databases opt for JavaScript-based editors that is the recognizable technology of the future. So, the best among the structural editors nowadays is Marvin JS, which is widely used in the application of Reaxys. The most exciting and commercially available program for drawing chemical formulas is Chem Draw, which is marketed by Cambridge Soft. The most recent version of this editor permits the user to search for the diagrams directly in SciFinder[13].

The commercial chemical databases of the resource are the most popular and most widely used web applications of Scopus, Reaxys, SciFinder and Web of Science (WoS), in which the above search technologies are possible and are more closely related to this article. The chemical databases are nowadays searched to give novel ideas for prime discovery. The comparison of the search possibilities of Reaxys, SciFinder and Web of Science sources were published in 2016 [14], and a comparison of two more chemically oriented sources - Reaxys and SciFinder was published by Jaroslav Silhanek[15]. In this paper, we will first describe the types of databases used in chemistry and the possibilities of the most important commercial tools. The authors chose some of the databases as the object of study on the assumption that these databases might provide the most informative and relevant results for a specific query. As the main source of the selected database for retrieving results from published journals, books, patents, conference abstracts, and other available relevant resources. After a quick description of several existing databases, we will also provide an overview of alternatives to freely available chemical resources, which in some cases, may replace the commercial resources. And finally, we will conclude by highlighting the weaknesses and shortcomings of the database as well as recommend the ways for their best possible utilization. The research criteria adopted were based on qualitative and quantitative characteristics of the database such as source, citations, searching and special features by analysing previous studies.

2. Experimental

The open Web compromises a rich pool of various chemical data sources if the user knows where to find out. It has been over many years since some emerging chemical databases were dominated by a handful of established players, the field has practically opened up to a variety of innovative newcomers. Although some of the original databases are no longer active, it is inspiring to see that several them continue to run and even flourish. It is of course more likely that still many more services will be created and some of them will become irrelevant in the coming years. The Internet now offers a varied range of free online chemistry databases, and this list is being continuously updated with new information and new entries. The following list summarizes some of the databases that are freely available for the users.

2.1. PubChem

PubChem is a public repository for information on chemical substances and their biological activities. It is regarded as the grandfather of all free chemistry databases, which search over 8 million compounds by a variety of criteria and is systematized as three linked databases viz. PubChem Substance, PubChem Compound, and PubChem Bioassay[16]. PubChem is a database of chemical molecules and their activities against biological assays. The National Center for Biotechnology Information (NCBI) maintains its system. PubChem can be freely accessed through a web user interface where millions of compound structures and descriptive datasets are freely downloaded via FTP. PubChem contains the descriptions of substance and small molecules having lesser than 1000 atoms and 1000 bonds. More than 350 database retailers add to the developing PubChem database. PubChem have a significant amount of literature-derived bioactivity data of chemical substances which are manually extracted from several thousands of scientific articles by data contributors such as ChEMBL and BindingDB and additionally, through integration of data from Drug Bank, the Hazardous Substances Data Bank and other databases[17]. The databases of these databases complement to the contents of PubChem.

2.2. Crystallography Open Database (COD)

Crystallography Open Database (COD) is an open-access collection of crystal structures of organic, inorganic, metal-organics compounds, and minerals, excluding biopolymers. This database is specifically designed to store information about the structure of molecules and crystals[18]. All data on this site have been placed in the public domain by the contributors. The COD can provide a link to CIF if there is a CIF available somewhere in the internet. The Crystallography Open Database has more than 360,000 entries and has various contributors, as well as contains CIFs as prescribed by the International Union of Crystallography[19].

COD has a website http://www.crystallography.net which provides proficiencies for all registered users to deposit published or unpublished crystallographic structures as personal communications or pre-publication depositions. Having such sort of a setup that enables extension of the COD database by several users simultaneously. It also increases the chances for growth of the COD database and may be considered as one-step towards creating a worldwide Internet-based collaborative platform committed to the collection and curation of structural knowledge. Each structure deposited into the COD generate a unique seven-digit number, called COD number, which identifies a particular illustration of a structure determination. In general, COD does not accept duplicate structures.

2.3. PubMed

PubMed is a freely accessible web interface (since 1997) designed to search for records located primarily in the MEDLINE database of references and abstracts. It comprises more than 28 million citations for biomedical literature from MEDLINE, life science journals, and online books[20]. Citations may include links to full-text content from PubMed Central and publisher web sites. PubMed also provides access to older references even from the print form of Index Medicus dating back to 1951 or earlier in addition to MEDLINE. This bibliographic database is indexed by journal entries and other primary sources related to medicine. There is also information about publications in the field of medicinal chemistry or biochemistry. The PubMed identifier (PMID) is the primary key used in PubMed to identify the unknown in this database. The tool provided in PubMed facilitates saving searches, filtering search results saving sets of references retrieved as part of a PubMed search, configuring display formats of search terms and the extensive range of further options. PubMed records with recent increases in activity.

2.4. ZINC

ZINC is a commercially available free database of compounds for virtual screening and this database has brought virtual screening libraries to a comprehensive range of structural biologists and medicinal chemists. It contains more than 35 million available compounds in ready-to-dock, 3D formats[21]. Due to its structure-based virtual screening, it has numerous significant successes in recent years and is nowadays a common technique in initial stage of drug discovery in many of the pharmaceutical companies. ZINC can be easily used for download using the website http://zinc.docking.org. It is currently built from the catalogues of ten major compound vendors in several common file formats including SMILES, mol2, 3D SDF, and DOCK flexi base format and the number of molecules in ZINC is continuously growing. This database has been designed in such a way that it organizes data relationally so that it remains compatible to attain the objectives of efficient loading, incremental updates, querying, and data subsetting. These steps make them fast and efficient. Though exporting subsets of the database can make them slow, but this problem has been resolved by exporting the molecule subsets from the database into ready-to-download compressed files, and database-intensive work is scheduled in batch mode. This totally bypasses the relational database and subsets are downloaded speedily once it is ready. The web-based interface is fast as well as supports moderately complex queries and users may search ZINC based on several criteria. The ZINC server enables users to upload and process their own molecules, as we often come across molecules such as positive and negative controls that we need to dock that are not part of the existing database[22]. Henceforth, ZINC is much useful for virtual screening by experts and non-specialists equally and assist more researchers to attempt computational ligand discovery.

2.5. ChemSpider

ChemSpider is an open access chemical structure database, which provide rapid text and structure search access to over 67 million structures from hundreds of data sources. ChemSpider is one of the chemistry community’s primary online public compound databases. ChemSpider serves data for tens of thousands of chemists every day and it lays the foundation for many important international projects to integrate chemistry and biological data, facilitate drug discovery efforts and help to identify new chemicals from under the ocean[23]. It is not just a search engine based on terabytes of chemistry data but also acts as a crowdsourcing community for chemists those have contributed their data, skills, and knowledge for the enhancement and curation of the database. Therefore, it can be said that ChemSpider seems like Wikipedia by promising participation and contributions from the scientific community. ChemSpider can link open- and closed-access chemistry journals, environmental data, PubChem, Chemical Entities of Biological Interest (ChEBI), chemical vendors, Wikipedia, The Kyoto Encyclopedia of Genes and Genomes (KEGG), and few other patent databases[24]. These links allow a ChemSpider user to collect information of their interest, such as from where to buy a chemical, chemical toxicity, metabolism data, and so on. Amassing this level of related information through a usual search engine like Google or Bing is a time-consuming process. Additional features have been added to each of the chemical structures within the database, such as structure identifiers like SMILES, InChI, IUPAC, and Index Names, as well as many physico-chemical properties[25]. ChemSpider also offers access to a series of property prediction algorithms. The user can access this database by browsing http://www.chemspider.com/. The ChemSpider homepage as it appears on the desktop has been shown in Fig. 1. The provider of this service has been the Royal Society of Chemistry (RSC) since 2009, which gives more value to other positive and useful services.

For the known compound, it provides extensive information like all its possible names and identifiers (both standard and nonstandard), experimental and calculated physicochemical properties, toxicity and biological activity data, spectra (NMR, IC, MS, UV-vis), publications, patents, etc. The information that is available depends on what has been gained from the original sources and the links to it are available. The role of ChemSpider is to get information about all the compounds available on the web at one central location, make it easy to search and standardize their structures and names. It also improves the quality of chemical sources by using automated control of the structure and manual management of collaborating experts as well as provides a platform for data input and storage. Additionally, it tries to make it easy to access all data using a web interface optimized for mobile devices, mobile applications, and web services for data capture. It does integrate data into the RSC publication using the first links and use validated chemical names to search in Google Scholar, PubMed and RSC books, journals, and databases.

What is ChemSpider?

ChemSpider is a free chemical structure database providing fast text and structure search access to over 67 million structures from hundreds of data sources.

Search by chemical names

- Systematic names
- Synonyms
- Trade names
- Database identifiers

Search by chemical structure

- Create structure-based queries
- Draw structures in the web page
- Use structure files from your computer

Find important data

- Literature references
- Physical properties
- Interactive spectra
- Chemical suppliers

Blog

Royal Society of Chemistry Renews Partnership with ACD/Labs to Continue Providing Industry-Leading Data to Worldwide Research Community

Behind the Scenes at ChemSpider

34 Million chemical structures

Figure 1. ChemSpider homepage as on desktop.

2.6. Google Scholar

Google Scholar is a freely available web-based search engine, available since 2004, that indexes the full text or metadata of scholarly literature through a range of publishing formats and disciplines. The indexed resources include online journals, conference papers, books, dissertations, thesis, patents, and any other significant literature. It is estimated that it contains approximately 389 million documents comprising articles, citations and patents which makes it the world's largest academic search engine in 2018 [26]. Google Scholar has now become indispensable for research and research dissemination that provides a systematized and instant process for users to build on through a sort of digital snowball for literature retrieval. The reason for the excel of Google can be attributed to its sophisticated natural language processing. In addition to the search, Google Scholar users are also able to create a personal profile with a list of their own publications and can generate census statistics and H-indexes like that of Web of Science. Nevertheless, if a user wishes to use a structured query in accordance to the field values in the bibliographic record or to find documents that have not been issued, it is preferable to resort to paid databases. The difficulties faced by the Google Scholar users are that they are not aware that when it is updated, includes old articles, as well as no suggestions are provided for limiting searches.

3. Results and Discussion

The three major commercial web database applications that are widely used in the field of chemistry are Scopus, Web of Science (WoS) and SciFinder. All the three databases contain extensive search options and are somehow remarkably similar in their chemical content as well as in their search mode, search effectiveness and interface. They have periodically undergone significant overhauling

and have intense competition between them. This competition has led to improvements in the services offered by them, which is, however, advantageous for users. As these databases are expensive, it is not feasible to have all these databases, therefore the scientific libraries must decide that which citation database will meet the requests of the consumers more effectively. Despite of the similarities between them still there are differences between them that are worth of a detailed analysis.

3.1. Scopus

Scopus is the Elsevier's largest abstract and citation database of peer-reviewed literature, which was launched in 2004. The literature covers more than 49 million records including scientific journals, conference proceedings, and books[27]. Scopus offers a complete summary of the global research output in the area of science, engineering, medicine, humanities, and social sciences. Scopus database is the leading searchable citation and abstract source for searching literature that is continuously expanding and updating. Scopus offers smart tools that have the sorting and refining features to track, analyze and visualize research of more than 27 million citations and abstracts dating back to 1960s[28]. Researchers across the globe believe that use of Scopus had positive influence on the research finding as it is easy to use, saves time as well as provides quality outcome. The content on Scopus is derived from over 5,000 publishers, which is reviewed by an independent Content Selection and Advisory Board (CSAB) and then selected for indexing in Scopus. The metadata that is provided by publishers includes the following: authors name, affiliations, document title, volume, issue, pages, year, electronic identification (EID), source title, citation count, document type and digital object identifier (DOI). This metadata is integrated to different websites and platforms, which provides more precise search and enables retrieval of scientific information. Scopus provides International Standard Serial Number (ISSN) for journals, conference series or book series for series publication and International Standard Book Number (ISBN) for one-time conference or book publication[29]. The overall view of the working pattern of Scopus is given in Fig. 2.

However, the coverage of a journal by Scopus may be discontinued for a certain period i.e. it has breaks for some journals whereas for some journals Scopus makes a partial coverage. Several studies can be found in the literature making detailed descriptions of the main features of Scopus and comparing the databases with the aim of assessing the number of citations obtained by a particular set of documents in each of them.

Studies have analyzed the set of journals covered by each database as well as their interface accessibility and usability compared with Scopus, from the point of view of the number of items included, and of testing the breadth of coverage. The rankings from Scopus and WoS match at the top and the bottom but deviate considerably in the middle positions[30]. If the user is aware with search devices such as drop-down boxes and check boxes, even for the beginner Scopus is easy to navigate. Scopus have some extraordinary features such as: it allows the user to go both forwards and backwards in time by linking to both citing and cited documents; it can link to the publisher's web site to view the document; citation accuracy is so accurate that 99% of citing references and citing articles matched exactly; can work in all the common web browsers like Chrome, Internet explorer or Mozilla.

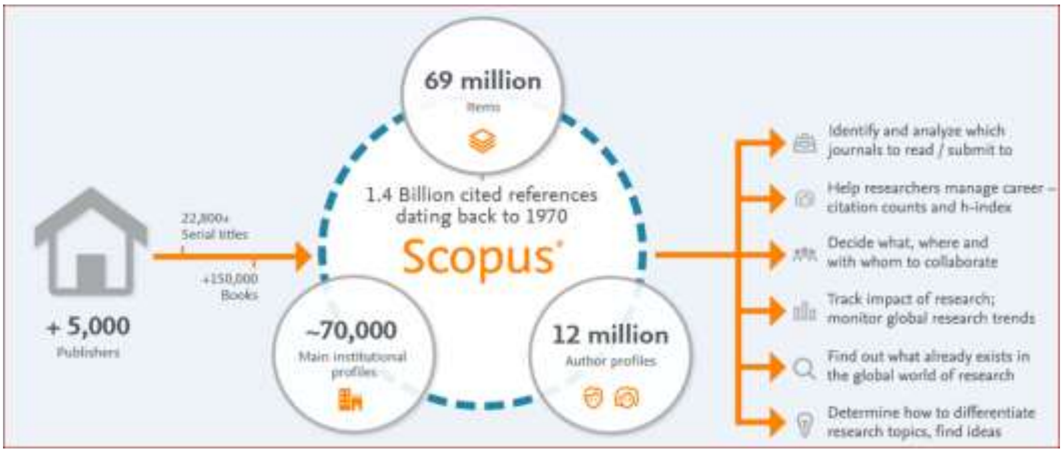


Figure 2. Working pattern of Scopus.

3.2. Web of Science

Web of Science is an ideal place to search the citation universe across subjects and across the world as it provides an access to the most reliable, integrated, multidisciplinary research that is connected through linked content citation metrics from multiple sources within a single interface[31]. As Web of Science adheres to a strict evaluation process, it assures that only the most influential, relevant, and credible information is included. The selection is made based on impact evaluations i.e. Impact factor (IF) that is a measure reflecting the yearly average number of citations to recent articles published in that journal and it includes open-access journals. Therefore, it allows the user to uncover the subsequent vast idea quicker. WoS connects the complete search as well as discover the process through Multidisciplinary Content; Subject Specific Content; Emerging Trends; Analysis Tools and Research Data. WoS precisely indexes the utmost significant literature in the world and has become the standard for research discovery and analytics. WoS links publications and researchers through citations and organized indexing in curated databases across every discipline. It uses cited reference search to track past research and monitor current developments for around 100 years of indexed content including 59 million records as early as 1898 [32]. WoS were originally created by the Institute for Scientific Information (ISI) and now is maintained by Clarivate Analytics. WoS enables the user to acquire, analyze, and disseminate database information in a timely manner and is possible due to the creation of a common vocabulary, called ontology, for varied search terms and varied data. Furthermore, these search terms generated relate information across categories. WoS platform provides access where the user can search individually or through a combination of topic, title, author or author ID, editor, conference, language, journal title, digital object identifier (DOI), year published, organization, address, document type, funding agency, grant number, accession number, and PubMed ID[33]. The Web of Science Core Collection, as illustrated in Fig. 3, consists of the following six online databases: Science Citation Index Expanded; Social Sciences Citation Index; Arts & Humanities Citation Index; Emerging Sources Citation Index; Book Citation Index and Conference Proceedings Citation Index. Apart from the seven citation indices listed, additionally two chemistry databases, Index

Chemicus and Current Chemical Reactions permit the creation of structure drawings, consequently allowing users to locate chemical compounds and reactions.

Key features of Data Citation Index (DCI) on WoS is to search directly through millions of records from hundreds of evaluated data repositories in the Sciences, Social Sciences, and Humanities[34]. Each DCI record links directly to the repository so that users can quickly access the associated research data. Citations to data sets are indexed so that the user can measure their impact as well as track their influence. The Data Citation Index offers a single point of access to research data from repositories across disciplines throughout the world. In this index, descriptive records are generated for data objects and linked to literature articles in the Web of Science. As data citation practices increase, the resource aims to provide a distinct picture of the full impact of research output, and act as an important tool for data attribution and detection. WoS has the most advanced features for citation analysis. It allows H-index to be honored that is now extensively used to assess the quality of the scholar and is able to search for multi-field quotes with respect to other databases. The newer WoS features provide search by the grant agency or the grant number. It is also possible to export the found export logs in various formats to a file or a web-based version of EndNote's personal bibliographic database. For subsequent import into another bibliographic database, it is appropriate to use the RIS structured export scheme, which is a recognized standard for these purposes. Controlling WoS is the easiest to learn with the help of a video tutorial, which are available to foreign operators.

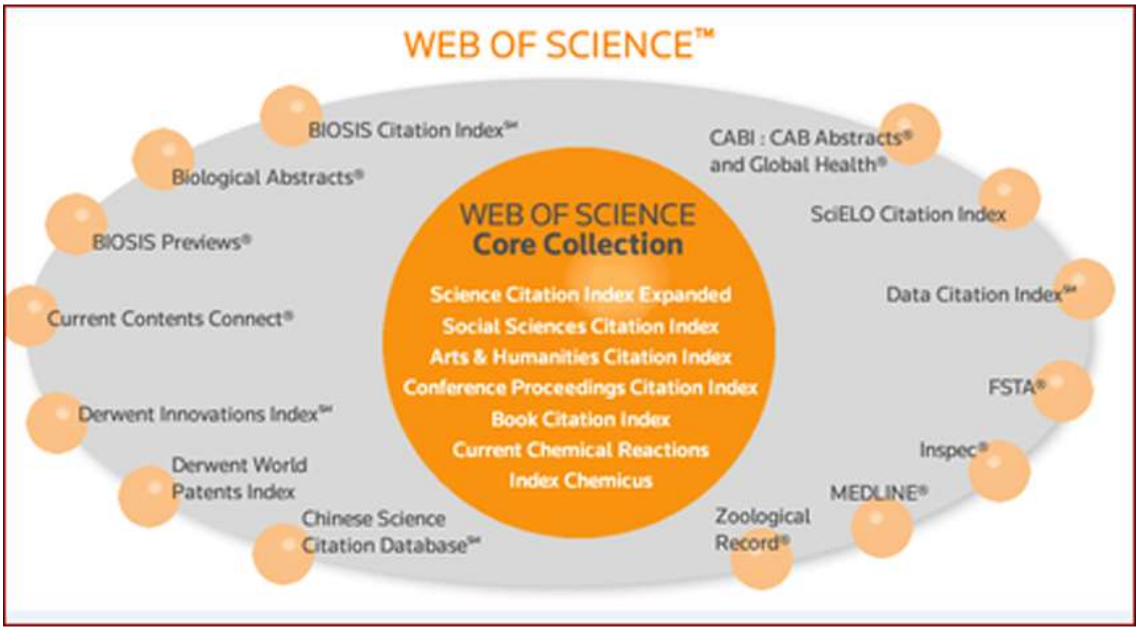


Figure 3. The Web of Science Core Collection.

3.3. SciFinder

SciFinder was launched by Chemical Abstract Service (CAS) in 1995 as a desktop application tool for Medals of Chemical Literature[35]. Today's application provides access to some databases produced by CAS, as well as to the freely available MEDLINE bibliographic database. SciFinder is a sophisticated search interface to six basic chemical related databases. CAS itself produces five of these databases. SciFinder Scholar is designed so infrequent searchers can explore the chemical literature, thereby eliminating the need to learn the intricacies of searching CAS. SciFinder offers easy, convenient, and prompt access to CAS REGISTRY, the standard for substance information, proposing more substances than any other single-source tool including organic and inorganic molecules, DNA, RNA, proteins, polymers and Markush structures[36]. On daily basis CAS scientists gather and investigate published scientific literature across the globe, creating the best quality and most up-to-date collection of scientific information in the world. Covering progresses in chemistry and linked sciences for the last 150 years, the CAS content pool empowers researchers, and information professionals with instant access to the trustworthy information required to catalyze innovation. SciFinder offer a direct search through the below mentioned database:

3.3.1. CAplus

The main Chemical Abstracts literature database of over 23 million references. It is a bibliographic database, which contains data from the most important chemistry journals for the CAS Source Index (CASSI), is available free of charge, where the user can search by CODEN, ISBN, ISSN, and naming or abbreviations for all sources used by CAS since 1907 [37]. The bibliographic records from this database are displayed in the SciFinder interface for relevant references to other CAS databases, and in most cases, references to the full texts of the document are also found.

3.3.2. CAS REGISTRY

It is a substance database containing information about all the compounds that CAS has ever been abstracted from the literature. It has a pool of more than 27 million organic and inorganic substances and 57 million bio sequences. Any previously unrecorded compound that is added to the database is assigned the new CAS Registry Number (CAS RN), which is a very wide-ranging identifier of chemical compounds, often used in chemical vendor catalogues[38]. For the most common chemicals, it is possible to search CAS RN by name of the compound or to find the name in a freely accessible web application operated by CAS - Common Chemistry[39]. If the user applies some forms and a structural editor from the SUBSTANCES section of the SciFinder interface, the results from the database will be displayed, and in each record, the user will be able to find the relevant links to the other CAS databases, including the CAS REGISTERS. Every day about 15,000 new compounds are added to the database. CAS REGISTRY serves as a universal standard for chemists worldwide.

3.3.3. CASREACT

It is a chemical information database that provides access to over 10 million reactions from the journal literature and patents. Most of the reactions are from the publications dating back to 1985, but the records published in 1840 can also be found[40]. If the SciFinder interface is used in the REACTIONS section, which allows search

only according to data entered in the structural editor, and the records from this database is shown. At present, the CASREACT database has more than 83 million records, and each day adds about 30,000 new responses.

3.3.4. CHEMCATS

It is a Supplier Chemicals Database, which lists suppliers of commercially available chemicals worldwide. For each commercially available compound, a link to its vendor that leads to this database is available[41]. However, only those suppliers who joins CAS CHEMCATS program are able to find it. Nevertheless, it is often possible to find a trusted supplier with a distinctly more favorable price than the usual suppliers. Naturally, the current price of a chemical is often quite different from what is reported in SciFinder.

3.3.5. CHEMLIST

It is a regulatory chemicals database. It includes chemicals that appear on a list of regulated chemicals (toxic, hazardous, etc.). If a compound is found in the CAS REGISTRY database, it is also contained in the CHEMLIST database. The appropriate links can be found in the compound record in the REGULATORY INFORMATION section[42]. Currently, this database contains more than 348,000 entries, and about 50 new substances are added each week that are accumulated from the extensive group of national and international regulatory lists and inventories.

4. Conclusions

The dimension of almost all chemical databases has increased manifold in the last many years so the search engines must be equally more powerful. The outline of this research is the usefulness of the databases for teaching, learning, and research as each chemical record retains the links to the original source of the material, thereby associating a micro attribution and these links let a database user source information of particular interest. Each of the commonly used chemical databases presented here has at least some overlap with each of the remaining ones, which means that each of these databases appears to have its own “niche”. The user, looking for a variety would like to give attention to each of them. These databases thus seem to be a valuable resource to the chemical community as they offer a large collection of compounds, either with related sample availability or with a diverse and unique structure set. As all the investigated databases developed over the years, the detailed results of these databases essentially signify a snapshot in time. The description reported here may give a useful overview relative to some of the most important large chemical databases available. In PubChem, unique chemical structures are extracted from the Substance database and stored in the Compound database that provides an accumulated interpretation of information for a given chemical structure. COD database establishes a worldwide Internet-based collaborative platform committed to the collection and curation of structural knowledge. PubMed provided a general description of PubMed including its content and unique characteristics. ChemSpider provides the variety of information of a given compound including physical and chemical properties, molecular structure, synthetic methods, spectral data, and systematic nomenclature for millions of compounds in a single Web site. The ZINC database provides 3D molecules in several formats compatible with most docking programs. Google Scholar helps to identify the collection of publications for a specific research topic. There is a high association between WoS and Scopus databases that allows searching and sorting the queries by anticipated parameters such as first author, citation, and institution, etc. regarding impact factor and h-index. SciFinder meets its goal of effectively exploring the scientific literature and the search results are mostly truly relevant and often astonishingly inclusive regardless of the level of complexity or syntax of the query. The database that ought to be used depends on the user and desired information. Therefore, the user must investigate the up-to-date condition of the specific database before establishing a decision of acquisition and usage of any of the databases presented here, as there may be changes in scope, configuration, vendor, etc. Libraries willing to subscribe the database should make their choice based on the needs of the library.

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