SUMMARY OF THESIS

"The Analysis of isotopic species of hydrogen from gaseous samples and liquid samples by CG and MS. The optimization of separating method CG".

The thesis had as main objectiv the analysis of isotopic species of hydrogen from gaseous samples by gas-chromatography and the analysis of isotopic species of hydrogen from liquid samples by mass-spectrometry. For the optimization of gas-chromatographic method was realized a study on Varian CP 3800 gas-chromatograph at different parameters.

The thesis includes two parts: a theoretical part and an experimental part.

The theoretical part includes two big chapters which presented two methods for analysis of isotope species of hydrogen: gas-chromatography and mass-spectrometry.

The thesis presents the analysis of isotope species of hydrogen from gaseous samples by gas-chromatography and the analysis of isotope species of hydrogen from liquid samples by mass-spectrometry, samples taken from Olt River, before and after industrial zone of Ramnicu Valcea town.

Hydrogen is the first element of periodical table and it has the simplest structure between all atoms of another elements.

There is three of hydrogen:

- The isotope $^{1}_{1}H$, protium, with his nucleus, H^{+}, it is protium;
- The isotope $^{2}_{1}H$, deuterium, $^{2}_{1}D$, with his nucleus, D^{+}, it is deuterium;
- Isotope $^{3}_{1}H$, tritium, $^{3}_{1}T$.

An isotopic mixture contains six isotopic species: H_2, D_2, T_2, HD, HT and DT. The six isotopic species are in equilibrium: $H_2 + D_2 \leftrightarrow 2HD$; $H_2 + T_2 \leftrightarrow 2HT$; $D_2 + T_2 \leftrightarrow 2DT$.

Tritium is presented in normal hydrogen in very small quantity, the order of $1:10^{-17}$, and deuterium is presented in normal hydrogen in percent of 0,015%.

The discovery of deuterium allowed instituting a new chapter in chemistry, very important and it is of isotopic substitution.

Normal molecular hydrogen is a mixture of three parts orthohydrogen and a part parahydrogen. At low temperatures, the ratio of parahydrogen is bigger.

Orthohydrogen and parahydrogen are different after the rotation sense of nucleus in around of own axes of two atoms which configuration the hydrogen molecule and, at orthohydrogen the nucleus are rotated in same sense, and at parahydrogen the nucleus are rotated in contrary sense.

This spine of nucleus is analog, though their characters, with the electrons spine, but the magnetic fields are dimmer.

Orthohydrogen and parahydrogen have same chemical properties, but are different through physical properties as specific heat and specters.

Normal molecular deuterium is a mixture 33% paradeuterium and 66 % orthodeuterium.

The first chapter – **"Gas-chromatography**" – contains five under chapters.

Gas-chromatographic separation of hydrogen isotopes have been reported in the literature dating from the late 1950's.

The gas-chromatography is a separating method of multicomponents mixture. It is based by the repartition of different components of mixture between a mobile phase and a stationary phase, full of the moving with different velocity of components taken by mobile phase lengthways stationary phase. This difference between migration velocity of the components is specifically natural chemical of these; depend on their physical-chemical properties.

There are many variants of chromatographic method classified after technique, work way, physical-chemical properties of phases etc. Between these, the most important variant (used for separating gaseous multicomponents, in particularly for the isotopic species of hydrogen) is gas-chromatography (or chromatography in gaseous phase). This variant, which used a gaseous mobile phase, attract after self, in obligatory way, the using of separating columns.

In the next containing of paper is an under chapter where are presented the retention parameters: adjusted retention parameters, corrected retention parameters and relative retention parameters.

In the next under chapter is presented the gas-chromatograph with description of his components parts:

1 – Bottle with carrier gas;

2 – Purification installation, regulation and measurement of pressure;

3 – Sample injector;

4 – Thermostat;

5 – Chromatographic column;

6 – Detector;

7 – Recorder.

The inert carrier gas, goes free by the bottle with gas under pressure, is passed through the purification installation, regulation and measurement of pressure, then through the sample injector, then elutes to the chromatographic column, where the components of the mixture are separated in individual components. At the come out of the column, these with carrier gas goes to detector, which give the signals transmitted to recorder.

In the next under chapter is presented the qualitative analysis and the quantitative analysis of gas-chromatography.

The qualitative analysis consist in identify the components in function by its properties and apparatus of analysis there are many methods for the identify the components of sample.

One between the simplest ways of identify is compared the retention parameters of sample components with of another unknown sample. It uses two variants of methods. The simplest variant consists in to compare the analyzed mixture chromatogram with unknown mixture chromatogram. A second variant consist in to compare the analyzed mixture chromatogram with the chromatogram of this mixture, where was added substances which are supposed that there are in the sample.

A good way very useful for to identify of mixture components is the using two or many detectors, one is universal detector, and specifically for a substances class.

The results evaluation of chromatographic analysis is made, in generally, in three steps:

1. Obtain of the so-called chromatogram.
2. The transforming of chromatogram in numerical dates concerning quantitative analysis what is reduced at the measurement of the height or area of picks. This can do manual or automatically integrators.
3. The correlation of obtained numerical dates from chromatogram, for to determine the qualitative composition of analyzed sample.

In all three steps interfere many errors; the reproducibility with is obtained the pick of the component is affected by the many possible errors, interlink by the constructive elements of chromatograph as: errors given by the way of sample injector, errors given by the variations of carrier gas flow, given irreversible retention in column of a fraction

of component quantity, errors interlink by the detector characteristics; the so-called integrated operation interlink errors in quantitative analysis.

The optimization of separating processes means, in fact, the founding of adequate values of different parameters of column for to obtain an optimal resolution and an optimal analysis time.

Gas-chromatography is applied with remarkable success in the analysis of components from variation domains, organics and inorganic.

The second chapter from theoretical part of this thesis is – **"Mass-spectrometry".**

This chapter contains three under chapters.

The mass-spectrometry used for the determination of molecular mass, the composition of substance, has at the base the analysis of the molecule through ionisation and the observation the behaviour in electric and magnetic field.

The apparatus used are the mass-spectrometers.

The mass-spectrometry became in the last time one of the most important methods of investigation in the study of structure of organic and inorganic substances or in isotopic analysis of elements.

The main components of mass-spectrometers are: pump system, ionisation room and source of electrons, focalisation lentils, cuadrupolar analyzer and the detector.

The sample is ionized in ions source, where is formatted the ions fragments. These fragments of ions are filtrated through a mass filter where are separated on the base of mass/charge report. The ions are detected by an electrons multiplication and amplified, formed measurable stream. This stream is converted in volumes concentration units.

The aspect of mass-spectrum depends in a big part by the mass-spectrometers used. If the ions detections does on photographic plate, mass spectrum is presented as a glass plate when can see the lines columns with different density.

Each line represents a figure of the slot out of ions source, the figure formatted by the different ions fascicles obtained by spectrometer. The density of these lines is a measure of the ions stream intensity.

In the way of the electrical detection of ions, mass-spectrum is given by a recorder and it is presented as the form of a curve.

The experimental part contains three chapters.

The chapter number three – **"The apparatuses used at the analysis of samples".**

This chapter contains two under chapters with the description of apparatuses used for the analysis of gaseous samples by gas-chromatography and liquid samples by mass-spectrometry.

For the analysis of gaseous samples was used Varian CP 3800 gas-chromatograph with the next characteristics:

- capillary column (inside diameter of column is: 0,32 mm), stationary phase is molecular sieve (film thickness of the column is: 30 μm), the length of the gas chromatograph column is: 50 m and 75 m;
- Cryogenic option for oven column: spraying LN2 with electro valve, minimum limit a temperature (-99 ^{o}C).
- TCD detector and Helium Ionization Detector;
- Pneumatic valves system is composed: one sampling/injection valve and 5 sampling valves. The sample loops can be calibrated on different volumes (sample loops 5 μL, 10 μL and 50 μL).

For the analysis of liquid samples was used mass spectrometer with magnetic sector with continuous flux DELTA V PLUS CF-IRMS.

Few characteristics of mass spectrometer:

- optic system: for high sensibility ions, uses an electromagnet with focalization at 90^{0};
- mass analyzer: monolith type without soldering, integrated heat system and controlled by software;
- vacuum system: turbo molecular pump (260l/s), with safety automat system;
- universal, triple collector;
- mass domain and resolution: mass domain 1 ÷ 96 daltoni at maximum acceleration tension and the resolution better than 110;
- The stability of system on mass scale :< 10 ppm.

The four chapter – **"Results and discussions"-** consists the next under chapters – **"The analysis of isotopic species of hydrogen by gas-chromatography"** and **"The analysis of isotopic species of hydrogen by mass-spectrometry".**

For the optimization of gas-chromatographic method was realized a study with Varian CP 3800 gas-chromatograph at different parameters.

Thus, were effectuated analyses from five etalon bottles which contains isotopic mixtures at different concentration:

1. etalon bottle of concentration 500 ppm D/D+H

2. etalon bottle of concentration 5% D/D+H
3. etalon bottle of concentration 20% D/D+H
4. etalon bottle of concentration 50% D/D+H
5. etalon bottle of concentration 99% D/D+H

The analysis was effectuated used for Varian CP 3800 gas-chromatograph, two detectors types: thermal conductivity detector and helium ionization detector.

To effectuate and to compare the analyses, on thermal conductivity detector, was used two different methods.

The analyses were effectuated at (-99^{0}C) oven temperature of column, temperature which represent the minimum limit of temperature to set the apparatus.

Also, worked at 100^{0}C detector temperature and the temperature on detector filament were fixed at 150^{0}C.

The carrier flow rate during the analysis, at (-99^{0}C) column temperature, was 9,9 mL/minute, the linear velocity was 54,57 cm/second at 28 psi pressure.

The retention time was between 12-14 minutes.

To effectuate and to compare the analyses on helium ionization detector worked with the chromatograph at different parameters: was used chromatographic columns with variable lengths (50 m and 75 m), the oven temperatures of chromatographic column were (-75^{0}C) and (-99^{0}C) and used 5 μL, 10 μL şi 50 μL sample loops.

The optimal method for the analysis of isotopic species of hydrogen resulted ago of this study, used the next components and the next parameters for working of gas-chromatograph:

- the helium ionization detector – temperature of detector is 200^{0}C;
- the length of the chromatographic column is 75 m;
- the sample loop is 5 μL;
- the oven temperature of chromatographic column is (-99^{0}C);
- the retention time is between 17-19 minutes.

For the using of these parameters, all isotopic species of hydrogen were presented, its are presented in same concentration as in the etalon bottle.

The analysis of liquid samples was realized on mass-spectrometer with magnetic sector with continuous flux DELTA V PLUS CF-IRMS.

Liquid samples were taken during a three seasons: winter, spring and summer, in months: January, April and August 2008, and the results were not influenced by three seasons, being in normal admissible limits.

The points for the taking of samples were: Raureni, point situeted before industrial zone of Ramnicu Valcea town and Tatarani, point situeted after industrial zone of Ramnicu Valcea town.

The chapter numer five is –**„General Conclusions".**

In this chapter was presented the most important conclusions resulted after the analysing of isotopic species of hydrogen from gasous samples by gas-chromatography and liquid samples by mass-spectrometry.