

DIRECT DISTILLATION TECHNIQUE FOR ACCURATE CARBON DIOXIDE QUANTIFICATION IN WATER

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Abstract

High-pressure solvent extraction (HPSE) has gained prominence in various industries, including chemical, food, and pharmaceutical sectors, owing to its numerous advantages. In this study, we explore the application of HPSE, particularly using CO₂ as the solvent, for the extraction of valuable compounds from marigold (*Calendula officinalis* L.), a plant with a wide range of applications in traditional medicine and modern formulations.

Conventional extraction processes, such as steam distillation and solvent extraction, often entail additional separation steps and exhibit lower selectivity when compared to CO₂-based HPSE. The unique characteristics of HPSE, including lower operating temperatures and reduced water content, contribute to the prevention of thermal degradation and hydrolysis of active compounds in the plant material. As a result, the extracts obtained through HPSE retain the integrity of active compounds and exhibit scents more akin to the original plant material.

Marigold, a well-cultivated plant in Europe and America, serves both ornamental and medicinal purposes. Traditional medicine has long employed marigold flowers to treat a variety of conditions, including inflammatory disorders of internal organs, gastrointestinal ulcers, diuretic and diaphoretic convulsions. Additionally, marigold extracts find applications in diverse pharmaceutical preparations, particularly in ointments for dermatological conditions such as ulcers, eczema, burns, and hemorrhoids.

Pharmacological studies of conventional marigold extracts, which include infusions, tinctures, and fluid extracts, have revealed that saponins, glycosides of sesquiterpenes, flavonoids, and triterpenes constitute the most vital constituents in these extracts.

This research aims to elucidate the potential of HPSE, specifically CO₂-based extraction, for preserving the integrity of marigold's bioactive compounds and enhancing the quality of the obtained

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extracts. The study will focus on the extraction process, the preservation of active compounds, and the sensory properties of marigold extracts. Moreover, we anticipate that this research will contribute to the development of more effective and sustainable extraction methods in the chemical, food, and pharmaceutical sectors.

1. Introduction

High-pressure solvent extraction (HPSE) is becoming increasingly popular in the chemical, food and pharmaceutical sectors. Extraction by means of CO₂, has been extensively studied in the last decade and has shown to be a good technique for the production of flavors and fragrances from plant materials.¹⁻³ Conventional processes, such as steam distillation, solvent extraction, *etc.*, often require additional steps, such as separating the extract and their selectivity is usually inferior to that of CO₂. Due to the lower temperature and low water content in HPSE, thermal degradation and hydrolysis are avoided. The extract obtained in this manner contains all active compounds unaltered from the plant and exhibits a scent more similar to the starting material.⁴⁻⁶ Marigold (*Calendula officinalis* L.) is a widely cultivated plant in Europe and America for ornamental and medicinal purposes. In folk medicine, the flowers of this plant are used to treat inflammatory conditions of internal organs, gastrointestinal ulcers, diuretic and diaphoretic convulsions.^{7,8} Calendula extracts are also used in diverse preparations, mainly ointments for the treatment of some dermatological conditions, such as ulcers, eczema, burns and hemoroides.^{9,10} Pharmacological studies of conventional marigold extracts (infusions, tincture, fluid extract) show that its most important constituents are saponines, glycosides of sesquiterpenes, flavonoids and triterpenes.

Rapid and accurate determination of carbon dioxide in aqueous samples is of industrial importance, especially in the beverage industry. As the CO₂ content in water and soft drinks, as well as in alcoholic beverages, is an important parameter for process and quality control, therefore, it is frequently measured. The measuring principle of the currently most popular CO₂ process analyzer is based on Henry's law, which states that the volume of a gas dissolved in a liquid is proportional to its partial pressure at a given temperature. During a measuring cycle a sample is drawn from the process stream and its volume is expanded in a measuring chamber. Due to the volume expansion a gas phase is generated in the measuring chamber. To accelerate equilibration of pressure and temperature between the liquid and gas phase, the sample is stirred with an impeller. In some measuring systems the equilibrium pressure is not reached within an acceptable time and must therefore be extrapolated. The CO₂ content is then calculated from the measured equilibrium pressure and temperature.

This measuring principle is inherently not selective for CO₂ as all other gases dissolved in the sample will also influence the gas pressure and thus cause interferences. A selective method for CO₂ determination would be of special interest in situations where in addition to CO₂ other gases are also contained in the liquid. In the present study, CO₂ determination under closed simple distillation system was investigated. The samples used were tap water, lemon juice (Kareem), milk (Nada), 7up, orange juice, Red Bull and Pepsi. The results obtained, with all of these products available in local Saudi market, are discussed in this paper.

2. Experimental

The experimental set up for the simple distillation is shown in figure1. The glassware used includes condensers, round bottom flask, heating mantle, thermometer, stopper, stands, and adapter, receiving flask and rubber hose.

The essential part of the procedure is as follows: Transferred 3ml of a sample into a round bottom flask and fitted with condensers as shown in figure1. The temperature of the heating mantle was slowly increased at a slow heating rate. When the temperature reaches to 50 and 60°C, the pressure gauge detects the CO₂ gas; the corresponding barometer readings were taken. The qualitative determination of CO₂ was done by bubbling the

outlet gas into calcium hydroxide solution. The whole process is repeated four times to ensure the reproducibility of the experiment and average values are reported in this paper.

3. Results and Discussion

From the pressure of CO₂ gas collected, the mass is calculated as follows.

$$\text{System Pressure} = \Delta h(\text{mmHg}) + P(\text{atm})$$

$$\text{CO}_2 \text{ Pressure} = \text{System pressure} - \text{Vapour pressure of water}$$

$$P(\text{CO}_2 \text{ mmHg}) = P(\text{system}) - P(\text{water})$$

$$P(\text{CO}_2 \text{ atm}) = P(\text{CO}_2 \text{ mmHg}) / 760 \text{ mmHg}$$

$$PV = nRT, \quad n = PV/RT, \quad n = \{P(\text{CO}_2) \times V(\text{system})\} / RT \quad n = \{P(\text{CO}_2 \text{ atm}) \times (0.962 \text{ L})\} / \{(0.0821 \text{ L.atm/mol.K}) \times (331 \text{ K})\}$$

$$\text{Mass of CO}_2 \text{ in vapour part of system} = \frac{\{M.W (\text{CO}_2) \times P(\text{CO}_2 \text{ atm}) \times (0.962 \text{ L})\}}{\{(0.0821 \text{ L.atm/mol.K}) \times (331 \text{ K})\}}$$

$$\text{Mass of CO}_2 \text{ in vapour part of system} = \{44.01 \text{ g/mol} \times P(\text{CO}_2 \text{ atm}) \times (0.962 \text{ L})\} / \{(0.0821 \text{ L.atm/mol.K}) \times (331 \text{ K})\}$$

$$\text{Mass of CO}_2 \text{ in vapour part of system} = P(\text{CO}_2 \text{ atm}) \times (1.558 \text{ g of CO}_2/\text{atm})$$

$$\text{Mass of CO}_2 \text{ in liquid part of system} = 1.5675 \times 10^{-3} \text{ g CO}_2$$

$$\text{The total mass of CO}_2 \text{ in the system} = \text{Mass of CO}_2 \text{ in vapour part of system} + \text{Mass of CO}_2 \text{ in liquid part of system}$$

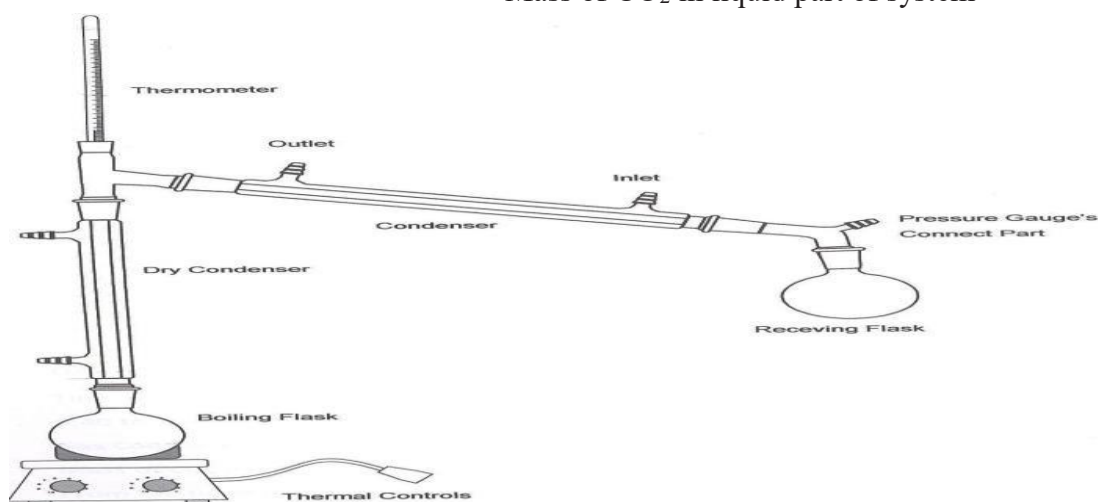


Figure 1. The experimental set up for the simple distillation

The results obtained with different samples are tabulated in table 1.

Sample	Average mass of CO ₂	Number of moles CO ₂	Calculated Molarity (M)
Tap water	1.32	0.021	0.298
Lemon juice(Kareem)	1.31	0.029	0.297
Milk (Nada)	1.30	0.029	0.296
7UP	1.33	0.030	0.302
Orange Juice (Nada)	1.31	0.029	0.298
Red Bull	0.31	0.029	0.299
Pepsi	1.33	0.030	0.303

Table 1. CO₂ content in different analyzed samples.

From this table it is clear that, different samples have different concentrations of CO₂. Among the soft drink samples available in the market, the CO₂ content is approximately the same.

4. Conclusions

From this study it can be concluded that CO₂ content of any liquid sample can be estimated by a simple distillation method. The accuracy of the method depends on maintaining a closed system, as any escape of CO₂ can affect the accuracy of the results. The amount of CO₂ estimation has not been previously performed using this direct method. It is known that CO₂ content varies with pressure of CO₂ gas above the liquid. So it is difficult to have a standard amount of CO₂ in solutions. This present study shows the usefulness of this novel method to measure the CO₂ content in liquids and the results are very interesting especially for carbonated soft drinks, as the one company have two different products, has the same amount of CO₂ content.

5. References

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