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Application of GC-NPD coupling with solid phase micro-extraction SPME for detection and identification of phosphine

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KEYWORDS
Phosphine ,
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sulfuric acid
(H2SO4).
Headspace

ABSTRACT:

Introduction: Commercial phosphine in Morocco is mainly used as a crop protection product and as a fumigant in the food and agricultural industry. It is used to eliminate harmful organisms such as insects, rodents and fungi that can damage crops, cereals and stored products.

In Morocco, commercial phosphine is sold by companies specialising in agricultural chemicals and pest control services. It is also widely sold in small-scale distributors (drugstores) and in urban and rural markets.

Objectives: Phosphine (PH3) is an inorganic compound with unique chemical properties and a variety of industrial and domestic applications. The study of phosphine is of crucial importance because of its potential for intoxication and its effects on human health. The aim of this study is to evaluate the use of headspace GC-NPD coupled to SPME for the detection and quantification of phosphine in various biological (liquid gastrointestinal) and food (vegetable and fruit) samples.

Methods: Headspace GC-NPD coupled with SPME offers many advantages, such as high sensitivity, high selectivity, rapid analysis and low sample consumption. However, this technique can present certain limitations, particularly with regard to the separation of non-volatile compounds and the complexity of optimising experimental parameters.

Results: The use of headspace GC-NPD coupled with SPME allows accurate detection and quantification of phosphine in various samples. The method described, using sulphuric acid (H2SO4) and gas chromatography with nitrogen flame panel detection (GC-NPD), allows reliable identification of phosphine in biological fluids.

Conclusions: This combination of GC-NPD and SPME offers high sensitivity, high selectivity and rapid analysis, while minimising the problems associated with analyst handling and the risks associated with sample consumption. This method allows efficient separation of sample components, as well as low sample consumption. However, limitations remain, such as the separation of non-volatile compounds and difficulties in optimising certain analytical parameters. Further research can be carried out to improve this method, particularly with regard to the separation of non-volatile compounds and the optimisation of parameters linked to the use of a SPME solid phase. In addition, other potential applications of the method can be explored, such as the detection of phosphine in other matrices and the adaptation of the method for more complex samples.

Introduction

Commercial phosphine in Morocco is mainly used as a crop protection product and as a fumigant in the food and agricultural industry. It is used to eliminate harmful organisms such as insects, rodents and fungi that can damage crops, cereals and stored products.

In Morocco, commercial phosphine is sold by companies specialising in agricultural chemicals and

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pest control services. It is also widely sold in small-scale distributors (drugstores) and in urban and rural markets.

1) Importance of phosphine .

Phosphine is a colorless, odorless and extremely toxic gas. Its chemical formula is PH3, with a molar mass of 33.997 g/mol. It consists of one phosphorus atom bonded to three hydrogen atoms. Phosphine's electronic structure gives it a number of unique chemical reactions and properties. It is used in the preparation of many industrial chemicals, such as pesticides and fungicides. Excessive exposure to phosphine can cause serious health problems, including respiratory problems, lung damage and neurological disorders.

1.1 Unintentional exposure to phosphine.

Unintentional exposure to phosphine can occur in work environments where it is used without appropriate precautions. Exposed persons may inhale the gas or come into contact with phosphine-contaminated liquids or surfaces.

1.2 Routes of absorption and distribution in the body

Phosphine can be absorbed mainly by inhalation, but also through the skin and orally. Once in the body, it is rapidly distributed in the tissues and can cause serious damage.

1.3 Symptoms and clinical signs

Symptoms of phosphine poisoning can vary depending on the concentration and duration of exposure. Common signs include breathing problems, headaches, dizziness, nausea and vomiting**.**

1.4 Short- and long-term effects

Acute exposure to high concentrations of phosphine can cause damage to the lungs, heart and central nervous system. In severe cases, this can lead to loss of consciousness, irreversible organ damage or even death. The long-term effects of chronic exposure to phosphine are not well documented.

2) Background and objectives of the study

Phosphine (PH3) is an inorganic compound with unique chemical properties and a variety of industrial and domestic applications. The study of phosphine is of crucial importance because of its potential for intoxication and its effects on human health. The aim of this study is to evaluate the use of headspace GC-NPD coupled to SPME for the detection and quantification of phosphine in various biological (liquid gastrointestinal) and food (vegetable and fruit) samples.

2.1 Advantages of using headspace GC-NPD coupled to SPME

Headspace GC-NPD coupled with SPME offers a number of advantages for the detection and quantification of phosphine. The method offers efficient separation of sample components, high detection sensitivity, rapid analysis and low sample consumption. It also offers high selectivity thanks to the specificity of NPD detection.

2.2 Détection and quantification of phosphine

Traditional methods, such as gas chromatography (GC) or mass spectrometry (MS), have been used to detect and quantify phosphine. However, these techniques have certain limitations, including long analysis times, high costs and calibration difficulties. The use of headspace GC-NPD coupled to SPME offers an interesting alternative to these conventional methods.

3) Basic principles of headspace GC-NPD coupled to SPME

3.1 Overview of GC-NPD

The Nitrogen Flame Panel Detector (GC-NPD) is used to detect and quantify phosphine. NPD is sensitive to the presence of nitrogen, phosphorus and other antioxidant compounds, such as phosphine.

3.2 Headspace principle

Headspace is a sampling technique that separates the volatile and non-volatile components of a sample. By heating, the volatile compounds are released into the headspace and then injected into the GC separation column.

3.3 Principle of SPME

SPME is a technique for extracting analysts from the sample onto a silica fibre coated with a stationary

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phase. This method allows efficient extraction of the volatile analytes present in the sample.

3.4 Advantages and limitations of GC-NPD and SPME techniques

Headspace GC-NPD coupled with SPME offers many advantages, such as high sensitivity, high selectivity, rapid analysis and low sample consumption. However, this technique can present certain limitations, particularly with regard to the separation of non-volatile compounds and the complexity of optimising experimental parameters.

4) Experimental methodology

A. Equipment required:

- Gas chromatograph (GC)

- Zero discharge photophoresis (NPD) detector

- Separation column (e.g. non-polar fused silica capillary column)

- fiber polymer 75 µm Carboxen-PDMS = Gases, volatile compounds

- Sample potentially containing phosphine

- Carrier gas (e.g. nitrogen or helium)

- Phosphine standards for calibration and blank for negative.

B. Procedure :

I. Color test (orientation test) :

1) Thaw liquid samples to be analysed.

2) Homogenize the sample

3) Take 1 Ml of the homogenized sample in a glass jar. *

4) Add 0.5 mL of sulphuric acid (10%).

5) Cover the jar with filter paper soaked in AgNO3 (saturated).

6) Leave to stand for 5 min

7) (appearance of a positive black color)_(no negative color)

II.GC-NPD/SPME identification test :

1) Thaw samples to be analyzed

2) Homogenize the sample

3) Take 1 Ml of the homogenized sample in a glass vial designed for headspace analysis. *

4) Add 0.5 mL H2SO4 (10%)

5) Hermetically seal the vial

6) Inject the GC-conditioned SPME fiber into the vial at optimum condition for 5 min.

7) Injection of the fibre after headspace adsorption at the GC-NPD injector.

*Must be prepared for each analysis sequence:

A negative test (staining test)

A positive and negative test (identification test)

- Phosphine standards for calibration and blank for negative.

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7) Injection of the fibre after headspace adsorption at the GC-NPD injector.

***Must be prepared for each analysis sequence:**

- A negative test (staining test)
- A positive and negative test (identification test)

A. Extraction of phosphine by SPME

Phosphine is extracted from the pressurized air sample in the vial by SPME, using a silica fiber coated with a specific stationary phase.

Biological fluid samples are treated with concentrated sulphuric acid (H2SO4) to release the phosphine from its bound form. A chemical reaction occurs, converting the phosphine into red phosphorus (P4) and phosphoric acid (H3PO4).

7.1 GC-NPD headspace injection

After extraction by SPME, the phosphine is injected into the GC-NPD headspace for separation and detection.

(PDMS : Polydiméthylsiloxane ; DVB : Divinylbenzène)

Types of fibre	Class of compounds
100 µm PDMS	Volatile and semi-volatile
65 µm carbowax-DVB	Polar compounds, volatile acids
65 µm PDMS-DVB	Volatile and semi-volatile
75 µm Carboxen-PDMS	Gases, volatile compounds

Figure 1 :Table of different type of fiber PDMS used for the test

7.2 Experimental conditions and parameter optimization

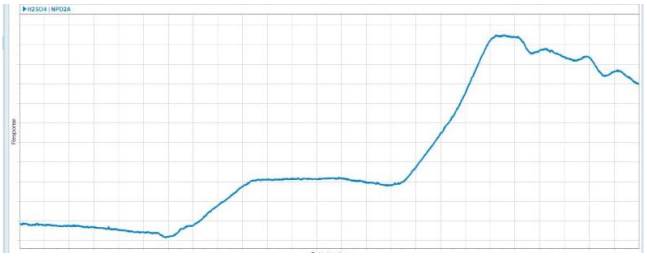
Experimental conditions, such as headspace temperature, carrier gas flow rate and GC separation time, are optimized to ensure efficient separation of the analysts.

7.3 Method calibration

The method is calibrated using phosphine standard solutions of known concentrations. This enables a correlation to be established between the phosphine concentration and the signal detected by the GC-NPD.

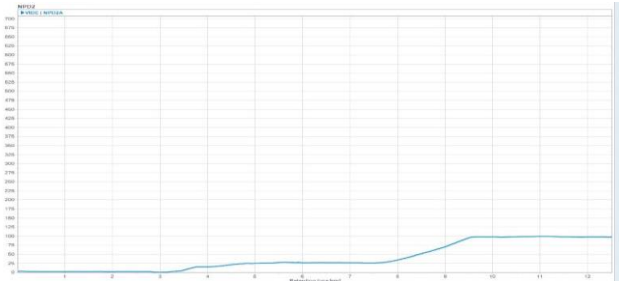
8) Results and discussion

8.1 Results obtained using headspace GC-NPD coupled to SPME



The results obtained show efficient separation of the sample components and sensitive detection of phosphine by headspace GC-NPD coupled to SPME.

Figure 2: GC-NPD/SPME results for a blank



(empty vial)

No peaks appear on the chromatogram with a relatively stable baseline with low fluctuations.

Figure3 : Result of GC-NPD/SPME analysis of 0.5mL H2SO4

The presence of H2SO4 in the thermal adsorption vial shows minor fluctuations in the baseline with no significant peaks displayed. H2SO4 will therefore have no impact on the peak retention times of the target molecules.

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The method is highly sensitive, allowing the detection of low concentrations of the target molecules.

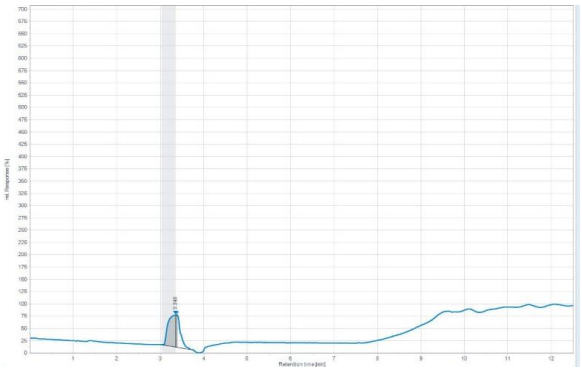

Figure 4 : GC-NPD/SPME result for a commercial phosphine sample (powder)

Exposing the SPME fibre to commercial phosphine alone produced an initial peak with an identified retention time. Corresponding to target molecule.

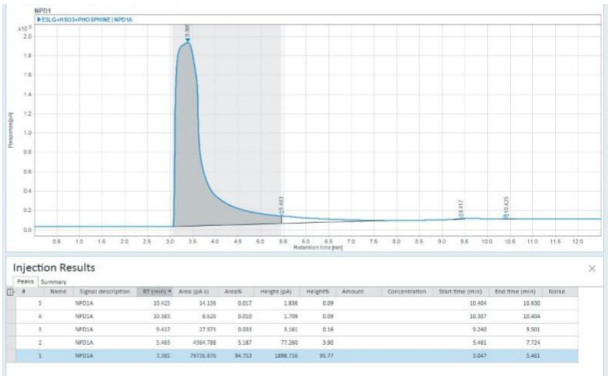

Figure 5 : Results of GC-NPD/SPME analysis for a Commercial Phosphine Sample

Commercial phosphine with 0.5mL H2SO4

SPME fibre to commercial phosphine mixed with 0.5 ml H2SO4 produced a high amplitude peak corresponding to the same retention time as initially identified. This corresponds to Our Target molecule.

concentrations of phosphine in the samples. In addition, the specificity of NPD detection gives the method good selectivity.

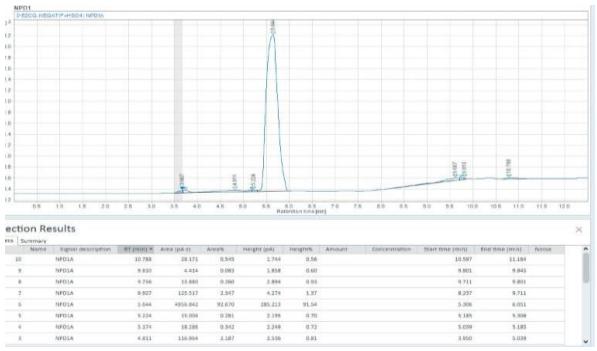

Figure 6: GC-NPD/SPME result for a phosphine-negative gastrointestinal fluid sample

SPME fibre exposure in a phosphine-negative gastrointestinal fluid sample yielded several peaks representing the composition of the matrix, with the absence of peaks representing the retention time of our target molecule.

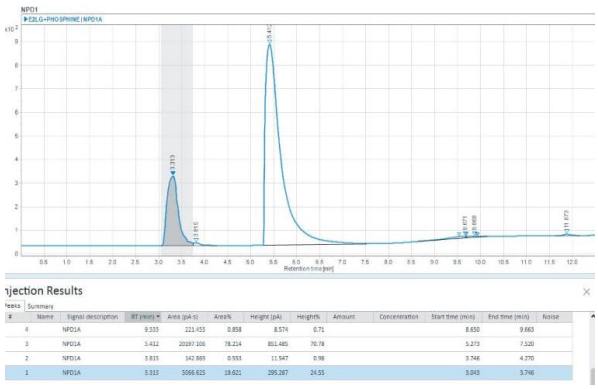

Figure 7 : GC-NPD/SPME results for a phosphine-positive controlled gastrointestinal fluid sample

SPME fiber exposure for a phosphine-positive gastrointestinal fluid sample yielded several peaks representing the composition of the matrix, with a moderate peak corresponding to the retention time of our target molecule.

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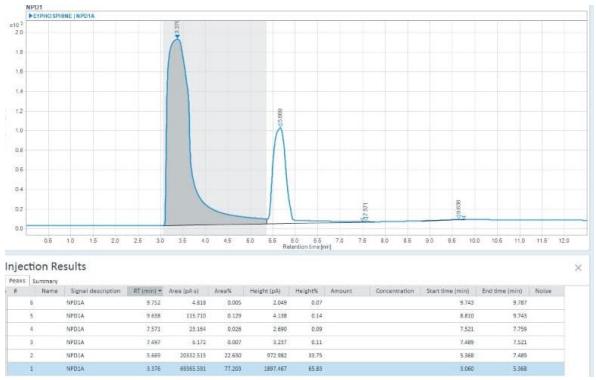

Figure 8 : GC-NPD/SPME results for a phosphine-positive gastrointestinal fluid sample with 0.5mL H2SO4.

SPME fibre exposures for a phosphine-positive gastrointestinal fluid sample homogenized with 0.5ml yielded several peaks representing the composition of the matrix, with one very pronounced peak corresponding to the retention time of our target molecule.

The method enables the precise qualitative and quantitative identification of phosphine in various samples, such as ambient air, soils and industrial chemicals. The identification of phosphine in biological fluids is achieved by comparing the retention times of the phosphine peak obtained from samples with those of phosphine standards. Phosphine standards are prepared to determine its presence or absence in samples**.**

8.2 Comparison with other phosphine detection techniques

- **Staining method**

Take 1 ml of the sample and homogenise in a glass jar to which 0.5 ml of sulphuric acid (10%) has been added. Cover the jar with filter paper soaked in AgNO3 (saturated) and leave to stand for 5 min.

- ✓ In the case of the appearance of a black coloration, the enchanting is considered positive for the presence of phosphine.
- ✓ In case of absence of coloration the enchantment is considered negative.

Staining test negative / Staining test positive

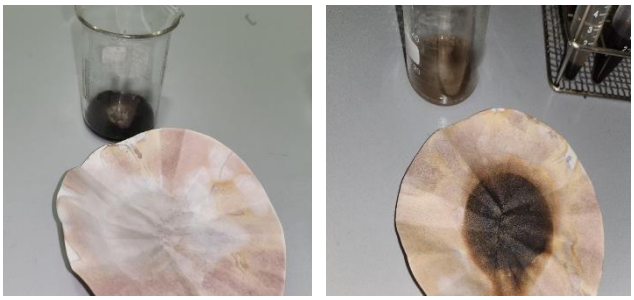

Figure 9 : Photography of the results of the staining test on two samples, one negative and one positive.

This method allows us to use a simple test to confirm the presence or absence of phosphine in the samples analyzed. This test is considered to be an analytical orientation test and is relatively reliable compared with GC analyses.

9) Applications and outlook.

9.1 Industrial applications of the method

9.2 The method has many industrial applications, such as monitoring air quality in production plants after phosphine treatment, and detecting contamination during the handling and storage of phosphine-containing chemicals. Although the method has many advantages, certain limitations are still present, such as the separation of non-volatile compounds for commercial formulations and difficulties in optimizing certain parameters. As the SPME extraction polymers and in this voice. Further research efforts can be undertaken to improve these aspects and define new extraction and identification methods.

Conclusion

The use of headspace GC-NPD coupled with SPME allows accurate detection and quantification of phosphine in various samples. The method described, using sulphuric acid (H2SO4) and gas chromatography with nitrogen flame panel detection (GC-NPD), allows reliable identification of phosphine in biological fluids. This combination of GC-NPD and SPME offers high sensitivity, high

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selectivity and rapid analysis, while minimising the problems associated with analyst handling and the risks associated with sample consumption. This method allows efficient separation of sample components, as well as low sample consumption. However, limitations remain, such as the separation of non-volatile compounds and difficulties in optimising certain analytical parameters. Further research can be carried out to improve this method, particularly with regard to the separation of non-volatile compounds and the optimisation of parameters linked to the use of a SPME solid phase. In addition, other potential applications of the method can be explored, such as the detection of phosphine in other matrices and the adaptation of the method for more complex samples.

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