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Reduced solvent and reagent sizes: effect on the carbonyl dinitrophenylhydrazone measurements at low concentrations

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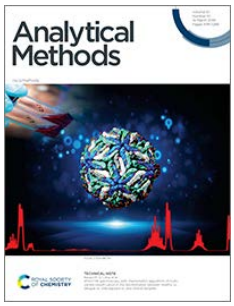

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This study helps to characterize the environmental quality of organic pollutants and their toxicity through analytical methods that maintain sustainability criteria in laboratory tasks. This type of contribution will undoubtedly be useful to share, transfer methodology and analytical support for related research and carried out in other disciplines. Analytical procedures that do not require sophisticated and expensive instruments continue to be of great interest in routine monitoring for many analytical laboratories.

ANSWERS

Comments to the Author

In this paper, the authors investigated "Reduced solvent and reagent sizes: Improved measurement of carbonyl dinitrophenylhydrazones by liquid chromatography", The results are interesting and promising, but lack in-depth analysis.

1) The quality of the figures is low and needs to be enhanced.

We have tried to modify the quality of the figures according to this recommendation. The figures have been recorded again with a *.tif* extension as recommended.

2) **The titles of the tables are not mentioned in the manuscript.**

In the revised document, we have entered the footer of each table in each Word document that includes the corresponding table. In the previous version, we entered the footnotes in *My author account* as Caption/Legend option and they did not appear in the pdf draft

3) **The authors have stated in the conclusion section that "The study contributes for the adaptation to more sustainable analytical methods to determine carbonyl compounds, simplifying the number of analytical steps while also decreasing time and costs. " Comparing determination methods in most situations, comes after calculating the limit of detection that must be comparable to previous works, was this the same case?**

The text has been modified to compare our detection limits (page6, line 48) with detection limits founded in literature

- "*In the case of cartridges eluted and DNPH concentrations of 400 µg mL^{-1}, the LOD ranged from 15 to 21 ng mL^{-1} (Table 1). These values agreed with those found recently in literature* [19-22]").
- *"Background values are well below the acceptable limits established by the TO-11A Method for a batch of user-prepared DNPH-coated cartridges* [2]"

4) **Validation of this method should be added in this work (repeatability, stability, selectivity and recovery of this method?)**

We greatly appreciate this recommendation to improve the paper. Indeed, the structure of the work was confusing and did not facilitate its follow-up with the reading. For example, although Table 1 is a compilation of the main analytical parameters obtained, it could lead to some lack of clarity in the presentation. Although we had already described the analytical quality parameters in the original document as indicated below, the text as a whole could be misleading.

1. Stability: Page 4: Lines54-56 ("Therefore, we selected the use of freshly DNPH solutions in a concentration not exceeding 500 µg mL-1 to avoid increases in the background levels").
2. Intermediate precision: Page 6, Line 22 ("intermediate precision was studied by comparing results of background levels of carbonyls among two DNPH devices and very different DNPH concentrations); Line 40 ("The coefficients of variation corresponded to 10, 21 and 25%")
3. Limits of detection and quantification: page 6, Lines 45-47 ("to estimate the corresponding limits of detection (LOD) and quantification (LOQ) as the sum of background plus three and ten times this value multiplied by rsdblank"); Line 48 ("For DNPH in solution with concentrations of 400 µg mL-1, LOD were calculated between 6 and 10 ng mL-1, while LOQ were between 12 and 19 ng mL-1. In the case of cartridges eluted and DNPH concentrations of 400 µg mL-1, the LOD and LOQ values ranged from 15 to 21 ng mL-1 and 26 to 41 ng mL-1, respectively")

4. Recovery: Page 7, Lines 18-19 ("The ratio between masses of measured carbonyl and those initially added were used as the efficiency value for hydrazone formation"); Line 31-32 ("For 300 µg as DNPH load, the results indicated complete hydrazone formation for the total mass of carbonyls tested (1.9, 3.8, 19 and 38 µg)
5. Selectivity: Indeed, no specific allusion has been made in the text to the selectivity of the method. The reason is that the chromatographic profile of DNPH hydrazones depends on the measurement chromatographic conditions and is usually good for formaldehyde and acetaldehyde. Acetone is limited by co-elution with acrolein. These results are in general depending on the instrumental conditions of measurement.

The text has been reorganized and rewritten to try to clearly visualize the quality parameters of analytical interest. Table 1 has been divided into Table 1 (Method precision and method detection limits) and Table 2 (comparison of calibration with commercial standards). Figure 3 has been added to illustrate efficiency of hydrazone derivatization depending on DNPH loading per cartridge.

5) **The authors should add a comparison table including (quantification limit and other important parameters).**

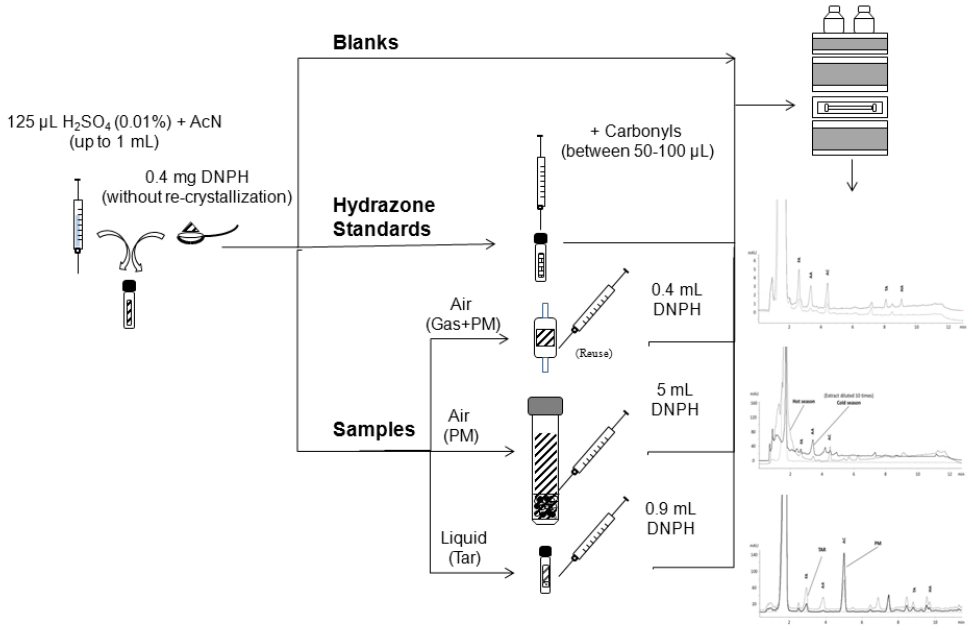
The text now includes mention of the lowest values found with respect to the limits considered acceptable according to the reference method (Method TO-11A). In addition, we have chosen to include a reference with recent bibliographic citations that indicate detection limits similar to those deduced in this work (Page 7, Line 3).

6) **The conclusion section is very brief and should be enriched.**

The text included in the "*Conclusions"* section has also been rewritten.

7) **English needs to be polished carefully, there are some mistakes**.

We also apologize for the mistakes that the work contained. We hope they have been removed



In this study, we proposed a method that simplifies the treatment of environmental samples to quantify the most abundant carbonyls by using reduced sizes of DNPH and acetonitrile. Exposure to acetonitrile and DNPH, waste production, and associated costs are reduced.

254x190mm (96 x 96 DPI)

Reduced solvent and reagent sizes: effect on the carbonyl dinitrophenylhydrazone measurements at low concentrations

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Abstract

This work aims to advance towards a more affordable laboratory work during sample treatment to determine carbonyl compounds by derivatization with 2,4-dinitropehylhydrazine (DNPH). The proposal is based on reducing DNPH and solvents. A simple addition of standard carbonyls in solution containing DNPH to prepare hydrazone standards is described and evaluated. Tedious recrystallization steps are avoided. Formaldehyde, acetaldehyde, acetone, tolualdehyde and hexanal, as carbonyl models, were quantified using DNPH concentration of 400 µg mL^{-1}, 3.8 mM H_2SO_4 and kept 24 hours at room temperature. Analytical coefficients of variation between 10 and 25% were found from the analysis of blanks under intermediate conditions (two different devices, very different concentrations of DNPH and analysis during two days). From these values of relative standard deviations and background levels, quantification limits were estimated between 15 and 40 ng mL^{-1}. The reduced reagent sizes allow the operator to better control the background levels in the use of DNPH, as well as being more cost-effective and easy to use. In short, it leads to a more sustainable adaptation of the classical method.

The versatility in analytical application was tested to estimate the levels of formaldehyde, acetaldehyde and acetone in very different types of environmental samples. In particular, outdoor and indoor samples were collected in filters and impregnated cartridges, respectively. Moreover, tars in 2-propanol and particulate matter from gasification processes were also tested.

Introduction

The use of DNPH combined with HPLC/UV has been considered a standard method to quantify carbonyl compounds for more than twenty years. Since 1996, the method EPA-8315A provides detailed procedures for the determination of carbonyl compounds in various matrices by derivatization with DNPH [1]. The method is based on the presence of an excess of DNPH to guarantee the complete formation of hydrazones in the sample using high volumes of sample and reagents. One of the main inherent disadvantages is the presence of impurities in the reagent and consequent increase in the background levels of certain carbonyls.

In 1999, the method EPA TO-11A implemented the use of cartridges impregnated with DNPH (DNPH-coated cartridges) for analysis of gaseous phase in air [2]. Although the method includes instructions for the preparation of DNPH-coated cartridges, the purchase of pre-coated DNPH cartridges is recommended to avoid tedious tasks for DNPH recrystallization and reduce background levels. Since then, they appear as very simple devices to collect carbonyls in the outdoor/indoor air both in active/passive mode, and using a wide variety of commercially available impregnated cartridges [3, 4]. These cartridges have short expiration dates and must be discarded after use. This "use and waste" of single-use products does not follow the current trend towards sustainable measures. Moreover, the demand for a large number of samples is common during environmental studies. This involves the need to purchase a large quantity of cartridges. There is the possibility of reusing the cartridges; however, such reuse of cartridges has been very scarcely addressed in literature [5]. One of the most recent cases is the work reported by Villanueva et al. [6] who give a detailed description to prepare and reuse air sampling cartridges from Radiello® passive sampler for Volatile Organic Compounds (VOCs), which are usually characterized in parallel with carbonyls. Besides the economic cost, exposure to chemicals during handling is risky. In the case of exposure by

inhalation to acetonitrile, it is verified according to exposure time and solvent concentration [2]. These health risks are clearly minimized when handling small volumes, such as 1 mL. Finally, from an environmental point of view, the use of more sustainable strategies such as reducing waste and promoting recycling is increasingly becoming a priority.

Among other drawbacks, derivatization with DNPH is complex and subjected to many factors that can easily lead to measurement errors. A lot of research has been done about it. For instance, the use of impregnated cartridges is associated with relatively low ketone capture efficiency [7], decomposition of DNPH with interference formation in presence of ozone [8], or alterations in the signal of hydrazones in presence of humidity [9] and dioxide of nitrogen [10]. During sample treatment, hydrazone formation can be influenced by changes in solvent composition, extraction time, temperature, solid/liquid ratio, and pH. The formation of isomeric 2,4-DNPHydrazones from asymmetric carbonyl compounds can cause also analytical errors [11]. These factors must be considered in advance to control where possible. Despite these limitations, it is a method that has been and continues to be widely used for the estimation of carbonyl concentrations.

Today, the demand for the determination of aldehydes and ketones is requested not only in air samples but in different types of sample matrices. Dissolved DNPH is used as a solvent in liquid-liquid extraction in the analysis of samples of atmospheric particulate matter [12], water, [13], biological [14], and complex matrix such as oil derived from biomass formed during pyrolysis process [15].

The main objective of this work is to present the results of experiments in which the sizes of the DNPH and solvents involved in the determination of environmental carbonyls have been reduced. This simple modification has advantages such as a significant decrease in background levels, one of the analytical limitations of DNPH method. On this basis, it is also proposed to simplify the preparation of hydrazone standards and coated cartridges. Analyses of samples collected in impregnated cartridges, aerosol filters, and liquid samples were carried out to verify their versatility in terms of analytical application.

Experimental

Reagents and standards

Deionized water, sulfuric acid (puriss. p.a. grade), and acetonitrile (HPLC gradient grade) from Romil Ltd (Cambridge, Grain Britain) were used for sample preparation and chromatographic analysis. 2,4-Dinitrophenylhidrazine (DNPH) was supplied by Sigma Aldrich (Deisenhofen, Germany). Cartridges 360 mg LpDNPH were supplied by Supelco.

Individual pure solutions of carbonyl compounds were supplied by the following manufacturers. Acetaldehyde (99.5%, 0.78 g mL^{-1}), acetone (99.7%), tolualdehyde (1,015 g mL^{-1}), and hexanal (0,814 g mL^{-1}) were purchased from Fluka (Buchs, Switzerland), while formaldehyde, two grades of the reagent in water solution were used (3.7-4%, Panreac, Barcelona, Spain and 34.5 %, Merck Darmstadt, Germany).

For the preparation of acidified acetonitrile DNPH solution, 0.4 milligrams of DNPH were dissolved in 1 mL of acidified acetonitrile (3.8 mM, H_2SO_4). The DNPH solutions must be freshly prepared and discarded after use. An aliquot of the DNPH solution was reserved as a blank control solution.

For HPLC calibration, two kinds of stock solutions were used:

- CARB Method 1004 DNPH Mix 2: a stock solution purchased from a commercial manufacturer (named as commercial standard), which contain among others, the DNPH hydrazones derivatives of formaldehyde, acetaldehyde, acetone, p-tolualdehyde, and hexanal in concentrations of 30 μg mL^{-1} (in acetonitrile) and it was supplied by Sigma Aldrich (Wyoming, USA). The working calibration standards were elaborated from serial dilutions with acetonitrile.
- A standard stock solution of DNPH hydrazones prepared in the laboratory. First, a standard stock solution containing a mixture of the selected carbonyls (in acetonitrile, 1 mL) at a concentration of 50 mg mL^{-1} of each of them was prepared. Standard mixtures from serial dilution with acetonitrile were then prepared from 0.05 to 50 μg mL^{-1}. Finally, working calibration standards of carbonyl hydrazone derivatives were elaborated by adding volumes of carbonyl standards between 50 and 100 μL, and mixing with acidic acetonitrile DNPH solution (up to 1 mL).

To ensure the efficacy of the derivatization reaction, the solutions were kept in darkness at room temperature for 24 hours. It is important to highlight the practice of each of these preparations in differentiated areas of the laboratory, without an exchange of syringes. Analysis of carbonyls at low levels requires rigorous control during the handling of vials, syringes, and solvents to assure minimal contamination. Blank contents for each set of around five sample or standard analyses should be determined

Concerning the refilling of coated cartridges, they were re-conditioned with 1 mL of acetonitrile twice, being then dried under nitrogen flow. Volumes of 200 μL and 150 μL of a freshly DNPH solution in a concentration of 1000 μg mL^{-1} were placed into the cartridge by resting the needle of the syringe through the ends. They were then dried under nitrogen flow, plugged in plastic caps, and wrapped in aluminum foil. As a guide, DNPH loading ranged from 250 to 350 μg per cartridge. For control purposes, DNPH chromatographic peak was also measured during analysis.

Sample extraction

Different types of samples were treated as follows:

- Samples collected on cartridges: Indoor measurements were performed in bedrooms of a conventional house at approximately 0.5 meters above the ground. The room was closed without activity during the sampling period (30 min., 1 L min^{-1}). Cartridges were eluted by using 1 mL of acetonitrile.
- Particulate matter (PM) sampled on quartz filters: Outdoor samples were taken at a rural site characterized by the high influence of biomass burning sources during winter [16]. Four samples were collected at 30 m^3 h^{-1} (24 h) using high-volume samplers (Digital DHA-80). In detail, the samples corresponded to two PM10 (aerodynamic diameter lower than 10 μm) and two PM2.5 (diameter lower than 2.5 μm) collected during hot and cold seasons (June and December, respectively). One--eighth filters were put into a 10 mL closed glass tube and 5 mL of acidified acetonitrile DNPH was subsequently added. The tube was several times vortex-agitated using an automatic shaker (Vortex 1-IKA, Staufen, Germany). After keeping 24 h in darkness and room temperature, 1 mL of extract was used for carbonyl analysis.
- Liquid samples from biomass gasification emission: Samples were taken from measurement stations during the tests at Biomass Gasification Pilot Plant (CEDER/CIEMAT). Sampling system has been previously reported [17]. In brief, impinger bottles filled with 2-propanol were used for bubbling the raw gas and collect the

tar samples of interest. Moreover, a thimble filter was used for particle collection, which was Soxhlet extracted in 2-propanol for analysis. For derivatization, 2-propanol extracts were diluted in a ratio 1/10 (extract/acetonitrile). Then, about 0.4 mg of DNPH and 125 µL of H_2SO_4 0.01% (3.8 mM) were added. The final volume was 1 mL.

In order to assure the formation of carbonyl hydrazone derivatives, reaction time was selected for 24 hours in darkness at room temperature before HPLC analysis (as discussed below).

HPLC/UV analysis

A series 1260 liquid chromatograph (Agilent, Waldbrom, Germany) equipped with a column from Agilent (Zorbax Eclipse XDB-C18, 5 µm, 150*4.6 mm) at room temperature and an ultraviolet detector (365 nm) were used for chromatographic analysis. The injection volume was 25 µL. The mobile phase rate was 1.4 mL min^{-1}. Gradient solvent systems were used by mixing acetonitrile/water (55:45 v/v) for 2 minutes and then programming up to 85% of acetonitrile in 8 min and keeping it there for 1 min. An equilibration delay of 2 min was applied prior to the next injection, being the analysis time of 13 min.

Quantification was performed using five-point calibration curves from commercial standard, covering the linear concentration from 0.025 to 5 µg mL^{-1}. Regression coefficients were above 0.9995. The analytical repeatability determined by analysis of commercial standard solutions (25 ng mL^{-1}) led to standard deviations below 5%. Analyte concentration should be in the middle of the calibration range of standards to avoid larger uncertainty derived from the calibration step. When this was not possible, a response factor based on a lower/higher concentration level of standard was applied.

Results and discussion

Results are presented as follows:

1. Optimization of DNPH concentration to reduce background levels. Evaluation of method precision and detection limits.
2. Comparison of calibration standards prepared in the laboratory and commercial calibration standards
3. Optimization of DNPH loading to prepare coated cartridges. Evaluation of recoveries
4. Applicability of the method. Analysis of real samples

Optimization of DNPH concentration to reduce background levels. Evaluation of method precision and detection limits.

The chemical analysis that excludes the sample or the standard (i.e. blanks) allows the estimation of the background levels, which can be limiting in the quantification of carbonyl compounds by derivatization with DNPH., The quality of the solvent [2], the concentrations of DNPH and acid in the working solution, and the reaction time are considered among the factors with significant influence on background content.

The presence of carbonyls in acetonitrile solvent has decisive drawbacks to control background contents, especially acetone. Several tests were performed with solvents from different suppliers, some of which should

indicate very high background levels. In detail, four DNPH blank solutions prepared from acetonitrile of different quality and distributed by four different suppliers were analyzed compared. The results obtained led to concentration levels of formaldehyde, acetaldehyde, and acetone below 10 ng mL^{-1} for three of them. The remaining one showed acetone levels increased by a factor of 25.

Regarding DNPH concentration, increases in blank levels over time have been associated with slow leaching of contaminants and impurities involved during analytical protocol [18]. To evaluate the influence of DNPH concentration on the background content, we analyzed several blank solutions with different DNPH concentrations. In detail, six blank DNPH solutions ranging from 400 to 800 µg mL^{-1}, kept at room temperature and acidified (H_2SO_4, 19 mM) were analyzed at 0, 24, and 96 hours after their preparation. The results indicated significant background increases according to the time elapsed when concentration was higher than 500 µg mL^{-1} (Figure 1). In particular, formaldehyde, acetaldehyde, and acetone were associated with up to 10, 3, and 7 fold increases the lowest value when DNPH concentration was 800 µg mL^{-1} and 96 hours after preparation.

Figure 1

The background levels were estimated from the analyses of different DNPH blanks (H_2SO_4, 3.8 mM) prepared in the laboratory: two solutions prepared by directly dissolving DNPH reactive in acetonitrile and eluting six coated cartridges with different DNPH masses. Table 1 compiles the results obtained for these background measurements by triplicate in which DNPH concentration ranged from 70 to 2300 µg mL^{-1}. As can be seen, the background levels of carbonyl hydrazones increased as the DNPH concentration increase, with background levels of 2-20, 3-13, and 5-25 ng mL^{-1}, for formaldehyde, acetaldehyde, and acetone, respectively (tolualdehyde and hexanal were no detected). These background values are well below the acceptable limits established by the TO-11A Method for a batch of user-prepared DNPH-coated cartridges [2]

To assess precision method, we consider more practical the use of blank measurements instead of spiked solution. From Table 1, the standard deviations of the blank solutions at different DNPH concentrations were pooled (RSD_{pooled}) applying the following equation:

$$RSD_{pooled} = \sqrt{\frac{\sum_{i=1}^{5}((n-1)\cdot rsd^2_{(blank\_i)}}{\sum_{i=1}^{5}(n-1)}}$$

Where "$rsd_{blank\ i}$" was deduced as the ratio "$sd_{blank\ i}$ /$average_{blank\ i}$" obtained for each studied DNPH device. The coefficients of variation corresponded to 10, 21, and 25% for acetone, acetaldehyde, and formaldehyde, respectively. In the case of tolualdehyde and hexanal, which not produced background responses, six solutions containing low concentrations (25 ng mL^{-1}) were analyzed and estimated to be around 5%.

These results also allowed us to estimate the corresponding limits of detection (LOD) and quantification (LOQ) as the sum of background plus three and ten times this value multiplied by rsd_{blank_i}, respectively. For DNPH in solution with concentrations of 400 µg mL^{-1}, LOD was calculated between 6 and 10 ng mL^{-1}, while DNPH concentrations leads to LOD ranged from 21 and 34 ng mL^{-1}. In the case of cartridges eluted and DNPH concentrations of 400 µg

mL^{-1}, the LOD ranged from 15 to 21 ng mL^{-1} (Table 1). These values agreed with those found recently in literature [19-22].

Table 1

We conclude to select the use of freshly DNPH solutions in a concentration not exceeding about 400 µg mL^{-1} to avoid increases in the background levels. It should not be forgotten that the mixing ratio between DNPH and carbonyls must ensure that the concentration of DNPH in solution is high enough to obtain complete derivatization. An additional advantage associated with reducing the DNPH concentration is the reduction in the amount of reagent supplied to the chromatographic system. Continuous supply of a significant amount of DNPH during chromatographic analysis results in a slow reduction in the life of the chromatographic column.

Comparison of calibration standards prepared in the laboratory and commercial calibration standards

Once selected the most suitable DNPH concentration below 500 µg mL^{-1}, we set out to prepare our own hydrazone-carbonyl standards in solution. The EPA recommended carbonyl hydrazone solids preparation protocol is very labor-intensive and time-consuming. The simplest method would be the direct addition of the carbonyl standard to the DNPH solution in acetonitrile. From a DNPH concentration of 400 µg mL^{-1}, carbonyl standards were added, as indicates in the "*Reagents and standards*" section (Experimental), to different DNPH solutions which contained an increasing concentration of H_2SO_4 (1.9, 3.8, 9.4, and 19 mM). Two series of experiments were carried out adding carbonyls at concentrations of 0.78 and 1.56 µg mL^{-1} and the analyses were compared after 2, 24, and 72 hours from preparation. Therefore, the influence of reaction time and acid content on the formation of carbonyl hydrazones was studied.

While the reaction of DNPH with formaldehyde, acetone, hexanal, and tolualdehyde showed a minor influence, the formation of acetaldehyde hydrazone clearly depended on reaction time and the concentration of H_2SO_4. Figure 2 represents the variation of peak area of acetaldehyde hydrazone (0.78 µg mL^{-1}) registered at different H_2SO_4 concentrations and reaction times. The same profile was obtained using 1.6 µg mL^{-1} of acetaldehyde. Tests carried out at a concentration of 1.9 mM of H_2SO_4 achieved yields of only 50% after up to six days from the preparation of the derivative. We selected as optimized conditions a concentration of 3.8 mM of H_2SO_4 and keeping at least 24 hours in the dark at room temperature. This is in agreement with other works, which also recommended analysis after 12-24 h [13, 23, 24].

On the other hand, the presence of low levels of DNPH reagent would generate competition between carbonyls due to differences in kinetics for the formation of hydrazones. Depending on the carbonyl compound of interest, the DNPH/carbonyl ratio should be investigated. For instance, Wang et al. [13] noted a mixing proportion of 100:1 to obtain derivatization of carbonyls such as methyl vinyl ketone, which is very unstable. In our case, to estimate the DNPH concentration and its consumption during the derivatization reaction, we consider the DNPH chromatographic peak as one more analyte.

Figure 2

This kind of preparation of hydrazone standards without prior preparation/recrystallization of solid hydrazone, as recommended by official methods[2], simplifies greatly the analytical procedure. However, the preparation of calibration curves of hydrazone by direct spiking in vial has been scarcely reported in literature [25].

Regarding instrumental analytical parameters obtained from calibration standards prepared in the laboratory,. quantification was performed using triplicate five-point calibration curves (0.025 -5 µg mL^{-1}) and correcting areas of chromatographic peaks for blanks. The analytical repeatability was determined by analysis of standard solutions of 25 ng mL^{-1}. Relative standard deviations were below 5%, except for formaldehyde, which corresponded to 10%. The instrumental limit of quantification (LOQ) was calculated as ten times the standard deviations and the values were about 10-15 ng mL^{-1}.

Secondly, we made a comparison between the results from the analyses of a commercial standard and those obtained after the analyses of standard elaborated in the laboratory. Commercial standards were prepared by dilution in acetonitrile of Supelco Carbonyl DNPH Mix 2 standard. Table 2 includes calibration parameters related to instrumental responses into the range 0.05-0.5 µg mL^{-1}, obtaining in general a good concordance. Only acetaldehyde and tolualdehyde indicated some differences. Results of acetone from commercial standards corresponded to measure the peak of Acetone+acroleine, so considering similar chromatographic response between both carbonyl hydrazones, the slope has been estimated as half.

Table 2

After studying the analytical variability and standard preparation, the analysis of some impregnated cartridges with and without spiking was carried out as follows below to check recovery parameters.

Optimization of DNPH loading to prepare coated cartridges. Evaluation of recoveries

To adjust the DNPH load per cartridge and its ability to ensure the derivatization of the carbonyls sampled in the air, we start from two premises, namely:

- Do not exceed a DNPH load of 400 µg mL^{-1} to avoid increases in background levels of the carbonyl.
- To consider a total mass of carbonyl of 10 µg as the capacity for analysis of ambient concentration levels (indoor/outdoor), according to the literature and considering a volume of 30 L of ambient air (table 3).

To check recoveries, two sets of experiments were initially compared using 300 µg and 100 µg as DNPH load and 1 mL of acetonitrile as a volume for desorption. Duplicate experiments were carried out by adding 1.9, 3.8, 19, and 38 µg as the –total mass of carbonyl compounds to assess the capacity of DNPH cartridges prepared in the laboratory. Regarding the volume of 1mL, we have only found one study that uses this elution volume [10]. Volumes of at least 2 mL are commonly used. The ratio between masses of measured carbonyl and those initially added were used as the efficiency value for hydrazone formation. The results led to incomplete derivatization of hydrazone-acetaldehyde (between 60- 80 %) when the analysis was carried out 2 hours after the addition, which is in agreement with results previously obtained during the standard preparation of hydrazones in solution. These observations would be related to the influence of DNPH concentration on the kinetics of hydrazone-acetaldehyde formation. The final results 24 hours after spiking are shown in Figure 3. In the case of using 100 µg as DNPH load and adding 38 µg as total carbonyl mass, the efficiency of the derivatization reaction was not complete. Consequently, to ensure derivatization capacity, we would consider in principle a limit of up to 20 µg of carbonyl total if DNPH load were 100 µg. For 300 µg as DNPH load, the results indicated complete hydrazone formation for

the total mass of carbonyls tested (1.9, 3.8, 19, and 38 µg). Regarding elution efficiency with a volume of 1 mL, a second elution did not report a signal for the investigated concentration levels. The chromatographic peak of DNPH was measured as an analyte to control DNPH consumption during derivatization.

(Figure 3).

Finally, we made a comparison with commercial cartridges. The main difference was the DNPH loading between coated cartridges. While DNPH loading in the cartridges prepared in the laboratory was about 400 µg/cartridge, the commercial cartridges have a DNPH loading 1000 µg/cartridge. The experiment was designed as follows: masses of 25 ng and 500 ng of each carbonyl were added to each device, corresponding as total added mass to 0.125 and 2.5 µg, respectively. The hydrazone-acetaldehyde peak in the laboratory impregnated cartridges required 24 hours to reach a stable peak area, while there was no variation over time for commercial cartridges. These results are consistent with the need for a higher concentration of DNPH to kinetically favor the formation of hydrazone from acetaldehyde. Stability tests by storing the cartridges even unwrapped individually in a desiccator for three days indicated an analytical variability within the estimated method precision (20%).

As Figure 4 shows, in general, a good agreement was achieved for both cartridges when the total mass of carbonyls added was 2.5 µg. However, some differences were found in the results corresponding to the tests with lower carbonyl mass. Considering the higher blank levels of commercial cartridges, these could lead to greater variability of the measurement at low concentrations.

Applicability of the method. Analysis of real samples

The applicability of the method for the environmental determination of carbonyls was tested on different sampling devices: DNPH cartridges, filters, and liquid samples. In detail, air samples were collected using cartridges impregnated with DNPH for the joint sampling of the two atmospheric fractions (gas phase and particulate matter), quartz fiber filters were used for particulate matter (PM) sampling and liquid samples were obtained in isopropanol from biomass gasifiers sampling train. Reflecting the versatility offered by DNPH analysis, three types of very different fields of application were selected, and which are currently of interest from an analytical point of view because they demand to expand the analytical characterization of organics. Thus, as an example, indoor pollution [22, 26] and biomass burning [27] are two fields that will continue to promote more work on the characterization of carbonyl compounds due to their impact on air quality.

Formaldehyde, acetaldehyde, and acetone are ubiquitous in indoor and outdoor environments, which generally exceed 70% of the total quantified carbonyls in ambient air [28]. A comparison among results and some of the more recently reported data on air measurements are summarized in table 2. The results lead to concentration levels found in literature. Sarigiannis et al [29] conducted a thorough review of literature from 1990 to 2008 of several organic compounds classified as priority pollutants to be regulated. Among them, carbonyls such as formaldehyde and acetaldehyde are included with concentration levels ranged from 10 to 50 µg m-3 and 15 to 18 µg m-3, respectively. These values agreed with those found in our study, although the comparison of the measured concentration levels requires a more detailed study. For example, it is necessary to know some parameters such

as the season of the year in which sampling was carried out. According to several studies [30-32], summer formaldehyde levels increase by a factor of 2 which would be coherent with influence from the outdoor air.

Concerning aerosols collected on filter samples, four PM samples were analyzed from a previous characterization study at a rural area affected by biomass burning pollution [16]. It is worth mentioning that the studies on carbonyl content in atmospheric aerosols using liquid-liquid extraction with DNPH and HPLC/UV have been scarcely reported in the literature. Among them, glyoxal and methylglyoxal have received some attention [12, 23, 33], whereas the most volatile carbonyls have been rarely measured. This lack of data partially reflects the difficulty of its measurement in particles [34], e.g., long-term filter sampling is associated with certain measurement limitations such as to not being able to perform a differentiated sampling by time band. Starting from our premise about the simplicity of the proposed method, the results from an analysis of particulate matter long sampled collected over a long time have a guide value on the expected levels.

Regarding aerosol samples, the results obtained in June are consistent with those reported in other rural areas of Spain. However, important differences were found from measurements performed in December, when an increasing factor of up to 90 is reached in the case of acetaldehyde. These results could be attributed to the contribution of biomass burning as a source of formaldehyde, acetaldehyde, and acetone to the atmosphere [35, 36].

As a third application case, formaldehyde, acetaldehyde, and acetone have been identified in biomass gasification product gases [37]. Solutions of 2-propanol corresponding to tars collected in impingers and the extract of particulate material were analyzed. It is necessary to highlight these 2-propanol solutions must be diluted at least 1/10 or changed solvent to acetonitrile. The use of acetonitrile as a solvent during the derivatization stage must be maintained to apply the same experimental conditions. Moreover, tests carried out directly with 2-propanol led to acetone levels in the blanks of up to 50 ppm. In this sense, the higher levels of acetone obtained in the analytical results of the tar samples (table 2) could be justified based on the contribution of the blank background from isopropanol (1/10). Therefore, these preliminary results need additional studies on the characterization of acetone from analysis of tar in 2-propanol. No bibliographic references have been found for comparison.

Table 3

Figure 5 includes representative chromatograms obtained from the analyses of each kind of sample, namely: an indoor air sample collected on an impregnated cartridge, outdoor aerosol samples collected on cold/hot seasons, and samples of tars and particles collected as product gases from biomass gasifiers. As can be seen, the chromatograms corresponding to the analysis of the particulate matter samples taken in winter were the most complex and with the highest contents of the carbonyl compounds investigated. Formaldehyde, acetaldehyde, and acetone were the most abundant. Concentrations of up to 1 μg mL^{-1} were in general measured, including the results obtained from 1/10 dilutions when necessary. Only the acetone measurements in the tar analyses reached up to 4 μg mL^{-1}.

Figure 5

Conclusions

This work addresses the analytical potential for determining carbonyls at ambient levels by modifying the classical DNPH method reducing reagents and less handling. In this work, we proposed to reduce derivatization reagent and solvent which leads to associated advantages such as avoiding tedious recrystallization stages as recommends classical method and greater technical autonomy for the fresh preparation of standards or impregnated cartridges.

A concentration of 400 µg mL^{-1} of DNPH has been found feasible to determine concentration levels up to 38 µg of the most abundant carbonyls in air, which are higher than the 10 µg usually measured according to the literature. We have estimated detection limits around 15-20 ng mL^{-1}, in agreement with other authors. Method precision was evaluated from analysis of blank samples and led to values of about 20%. These results deduced from blank analyses have an added value to understand the final measurement variability and comparability among different measured concentration values.

The risks for contamination and exposure to chemical substances during handling are also significantly reduced. Moreover, hazardous waste generated during sample treatment, time, and economical costs are also decreased. Finally, to show its versatility in analytical application, preliminary results are included on the estimation of concentration levels of formaldehyde, acetaldehyde, and acetone in samples from three different fields.

In summary, this paper contributes to the adaptation to more sustainable analytical methods to determine carbonyl compounds, simplifying the number of analytical steps while also decreasing time and costs.

CRediT authorship contribution statement

Susana García Alonso: Formal analysis, Resources, Investigation, Validation, Wrhiting-original draft. **Ana María Bernal Páez**: Methodology, Formal analysis, Validation. **Rosa María Pérez Pastor**: Conceptualization, Supervision, Writing-review & editing.

Conficts of interest

The authors declare there are no conflict of interest regarding the publication of this paper.

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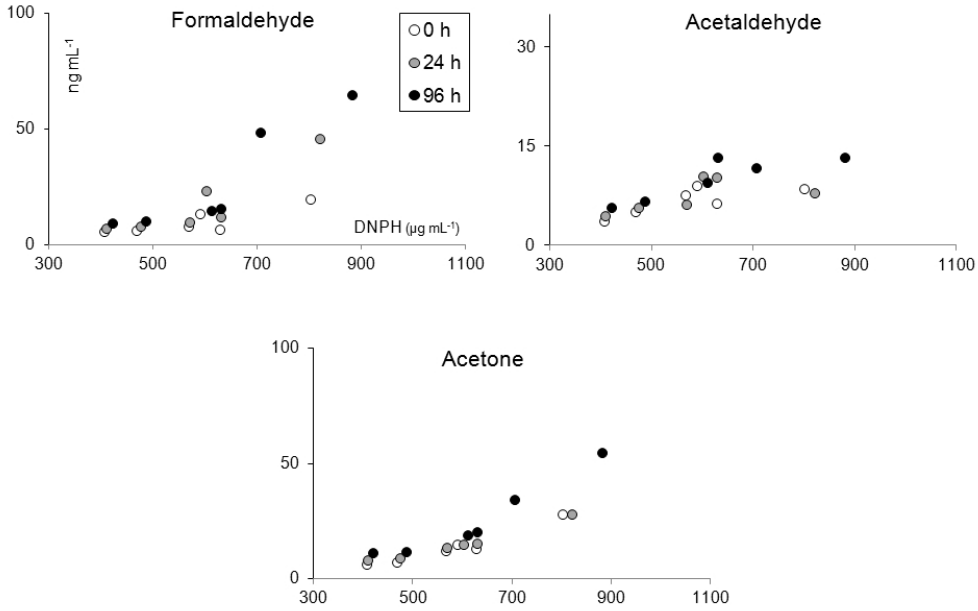

Figure 1- Background levels at various DNPH concentrations and elapsing up to three days from preparing of DNPH solution.

254x190mm (96 x 96 DPI)

Device		Solution (n=10)	Solution (n=8)	Cartridge (n=12)	Cartridge (n=6)	Cartridge (n=6)
DNPH (μg mL^{-1})		399±2.8	2301±87	69±14	285±8.0	430±9.9
Formaldehyde	Blank (ng mL^{-1})	5.6±1.4	20±4.9	2.3±0.59	3.2±0.33	12±3.2
	Pooled RSD (%)			24		
	LOD/LOQ (ng mL^{-1})	10/19	34/68	4/8	6/11	21/41
Acetaldehyde	Blank (ng mL^{-1})	3.9±0.83	13±3.4	3.2±0.79	4.8±0.28	9.2±1.0
	Pooled RSD (%)			21		
	LOD/LOQ (ng mL^{-1})	6/12	21/40	5/10	8/15	15/28
Acetone	Blank (ng mL^{-1})	6.5±0.55	25±1.1	4.9±0.60	6.6±0.85	13±1.0
	Pooled RSD (%)	10				
	LOD/LOQ (ng mL^{-1})	8/13	32/49	6.5/10	9/13	17/26
Tolualdehyde	Blank (ng mL^{-1})			5		
	Pooled RSD (%)			5/10		
	LOD/LOQ (ng mL^{-1})					
Hexanal	Blank (ng mL^{-1})			6		
	Pooled RSD (%)			5/15		
	LOD/LOQ (ng mL^{-1})					

Table 1 - Method precision and method detection limits: Background levels measured from blank solutions prepared by dissolving DNPH reactive (*Solution*) and those from eluting DNPH impregnated cartridge (*Cartridge*). Limits of Detection and Quantification (LOD and LOQ, respectively) expressed as ng mL^{-1} and obtained from blank analyses.

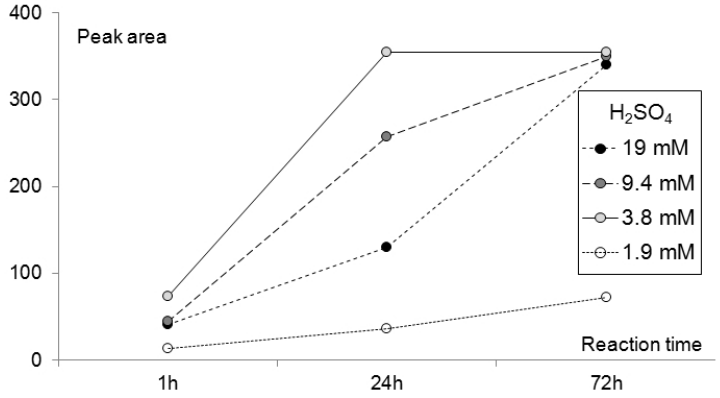

Figure 2 - Influence of H_2SO_4 concentration and preparation time on acetaldehyde_hydrazone measurements: variation of peak areas using a DNPH concentration of 400 µg mL^{-1}, acetaldehyde concentration of 0.78 µg mL^{-1}, and different concentrations of H_2SO_4 after up to three days from preparation.

254x190mm (96 x 96 DPI)

	Commercial standard		Standard prepared in Lab	
	Regression curve	Repeatability (%)		Repeatability (%)
Formaldehyde	A=563cc-3.99 (0.998)	5.0	A=585cc+8.80 (0.9998)	10
Acetaldehyde	A=449cc-2.50 (0.9993)	3.0	A=618cc+4.63 (0.9999)	2.5
Acetone	*A=760cc-5.85 (0.9994)	3.0	A=378cc-2.14 (0.9994)	5.0
Tolualdehyde	A=190cc-1.29 (0.998)	5.0	A=222cc+1.40 (0.9999)	3.0
Hexanal	A=206cc+1.15 (0.9999)	8.0	A=211cc-1.30 (0.9991)	5.0

Table 2 - Parameters of calibration estimated from the analyses of a commercial standard, and standards prepared in the laboratory. Linear calibration are expressed as Peak area= m*·concentration+b (R^2) in the range from 0.025 μg mL^{-1} to 0.5 μg/mL^{-1}

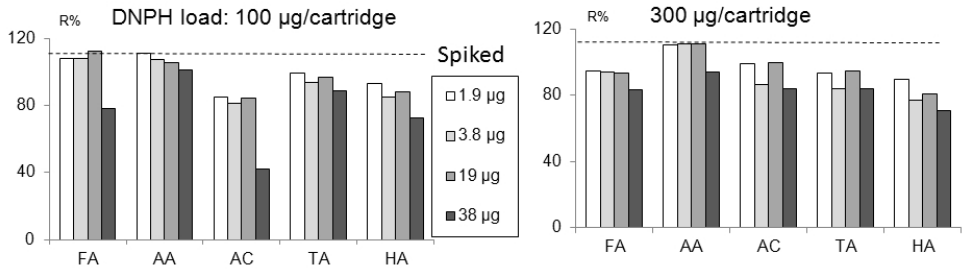

Figure 3 - Efficiency of hydrazone derivatization depending on DNPH loading per cartridge. The abbreviations correspond to formaldehyde (FA), acetaldehyde (AA), acetone (AC), tolualdehyde (TA) and hexanal (HA).

254x190mm (96 x 96 DPI)

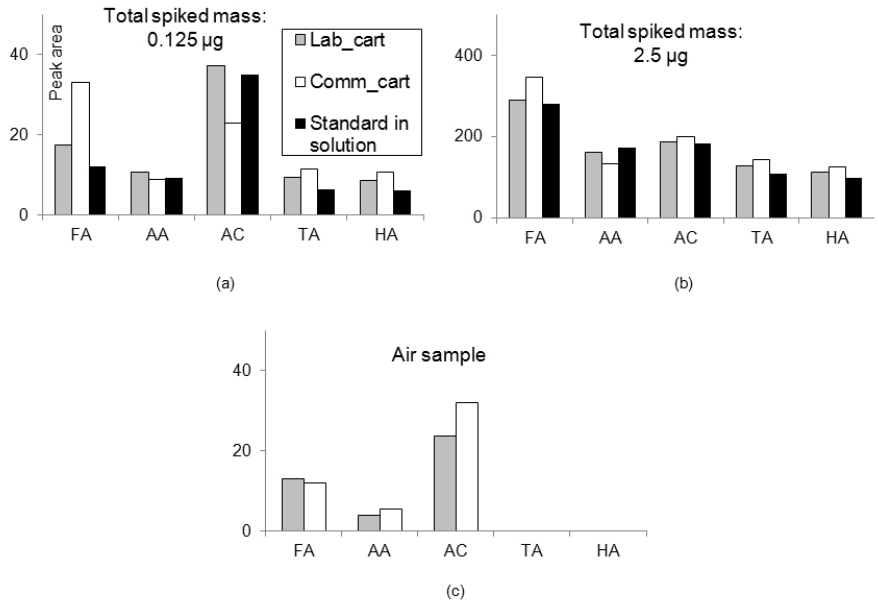

Figure 4 – Comparison of peak areas corrected for blanks between cartridges impregnated in the laboratory (Lab_cart) and commercial cartridges (Comm_cart) spiked with (a) a total mass of carbonyl standards of 0.125 µg, (b) a total mass of carbonyl standards of 2.5 µg, and (c) an air sample collected in parallel in the laboratory. The abbreviations for carbonyls are detailed in Figure 3.

254x190mm (96 x 96 DPI)

Air sample	Device			Sampling site (Indoor/Outdoor)	FA	AA	AC	Ref
	Cartridges	**PM filters**	**Liquid samples**					
PM+gas	Sep-Pak DNPH-silica (Waters)			Fortaleza, Brazil (I, µg m^{-3})	(1-82)	(1-8)	(1-234)	36
PM+gas	Sep-Pak DNPH-silica (Waters)			Guangzhou, China (I, µg m^{-3})	(2.6-7.6)	(2.4-4.6)	(7.2-15.5)	37
				Guangzhou, China (O, µg m^{-3})	(2.2-8.6)	(5.5-6)	(6.1-11)	
PM+gas				Hong Kong, China (I, µg m^{-3})	(10-48)	(1-7)	9.9	38
				Hong Kong, China (O, µg m^{-3})	(4.3-14)	(1.8-5.3)		
PM+gas	Sep-Pak DNPH-silica (Waters)			Colombo, Sri Lanka (I, µg m^{-3})	(3-8)	(3-4)	(1-3)	39
PM+gas	DNPH cartridges re-coated in lab (n=6)			Madrid (I, µg m^{-3})	(21-30)	(5-10)	(5-9)	This work
PM		Glass fiber (1.13 m^3)		Bus station (ng m^{-3})	(7-28)	(28-55)		40
				Tunnel	(7-23)	(27-89)		
PM		Glass fiber		Mainz,Germany				41
				Urban, (ng m^{-3})	65			
				Rural (ng m^{-3})	40			
PM		Quartz fiber		A Coruña, Spain				42
				Industrial,(ng m^{-3})	(0-10)	(0.33-2.7)	(0-2.5)	
				Rural, (ng m^{-3})	(0-14)	(0.15-3.0)	(0-4.8)	
PM		Quartz fiber (80-94 m^3) (n=4)		Rural area of Spain (ng m^{-3})				This work
				December	65	(545-625)	(20-50)	
				June	(7-10)	6-7	(20-25)	
TAR			2-Propanol tar solution (n=1)	Assays biomass gasification (µg mL^{-1})	7.5	5.2	20	This work
			PM_soxhlet extract (n=1)		2.5	0.15	39	

Table 3 - Formaldehyde, acetaldehyde, and acetone measurements obtained from different types of samples for comparison: ambient air (published in the last five years), particulate matter (with little data found in the literature), and tar solutions (no references found). The number of samples tested and the range of carbonyl concentrations are indicated in parentheses.

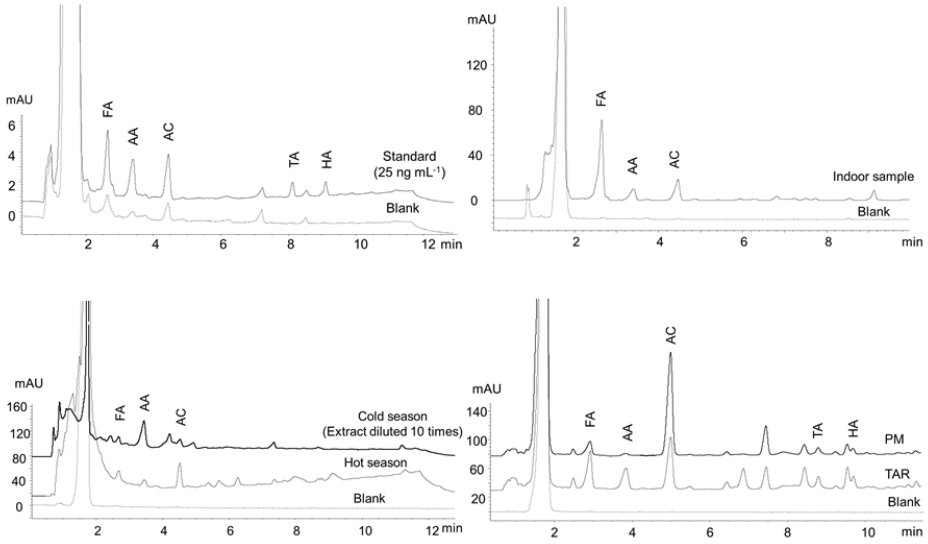

Figure 5 - Representative chromatograms registered from the analyses of samples from simplest to most complex matrices: (a) blank DNPH solution (400 µg mL^{-1}, 3.8 mM H_2SO_4) vs a standard containing 25 ng mL^{-1} of carbonyls, (b) an indoor air sample(30 L) collected on the impregnated cartridge (c) outdoor aerosol samples (~90 m^3) collected on filters during hot/cold seasons (d) product gas samples in 2-propanol solution (tar) and particles (PM) from biomass gasifiers. In dotted lines chromatogram registered from blank analyses and the abbreviations for carbonyls are detailed in Figure 3.

254x190mm (96 x 96 DPI)