

# **Breakthrough study for Waters, Sep-Pak<sup>®</sup> Vac 6cc (500 mg) Porapak<sup>®</sup> RDX cartridges for the retention of nitroglycerin**

Isabelle Poulin  
DRDC Valcartier

Marianne E. Walsh  
Alan D. Hewitt  
ERDC/CRREL

**Defence R&D Canada – Valcartier**

Technical Note  
DRDC Valcartier TN 2012-073  
November 2011

Principal Author

---

Isabelle Poulin

Defense Scientist, Energetic Material Section

Approved by

---

Marc Lauzon

Energetic Material / Precision Weapons Section Head

Approved for release by

---

Christian Carrier

Chief Scientist

- © Her Majesty the Queen in Right of Canada, as represented by the Minister of National Defence, 2011  
© Sa Majesté la Reine (en droit du Canada), telle que représentée par le ministre de la Défense nationale, 2011

## Abstract

---

Analysis of water samples from military ranges and training areas as well as from explosive manufacturing plants is common. Water samples can come from groundwater wells, lakes, streams, rivers and ponds. The preconcentration of explosive materials from these aqueous solutions is necessary to allow system compatibility (i.e. some analytical systems can process samples in organic solvent) and to ensure that the concentration are above detection limit. Preconcentrating the sample is done using a Solid Phase Extraction cartridge. The experiments described in this note were aimed at determining if it is possible to extract a volume larger than the common 1L or if breakthrough happens when using the standard cartridge for energetics (Waters SepPak Porapak RDX (500 mg)). Nitroglycerin (NG) was chosen as the analyte and it was analyzed using a liquid chromatography (HPLC) system with dual wavelength detector. For a 1 mg/L NG solution, results show that the retention decreases slowly with the increasing volume processed on the cartridge, after 2 L, the retention of NG was still over 96%, and after 4-L, the retention is still over 86%.

## Résumé

---

L'analyse d'échantillons d'eau provenant de sites d'entraînement militaires et d'usines de fabrication d'explosifs est fréquente. Les échantillons proviennent de puits pour l'eau souterraine, de lacs, de ruisseaux, de rivières et d'étangs. La préconcentration des matériaux énergétiques contenus dans ces solutions aqueuses est nécessaire pour assurer la compatibilité avec les systèmes d'analyse (certains systèmes ne peuvent traiter que des échantillons dans un solvant organique) et pour assurer que les concentrations détectées soient au-dessus de la limite de détection des appareils. La préconcentration des échantillons est effectuée par l'utilisation de cartouches d'extraction en phase solide. Les expériences décrites dans cette note visaient à déterminer s'il est possible d'extraire un volume plus gros que le 1 litre habituellement disponible ou si une percée est observée lors que les cartouches régulières pour les matériaux énergétiques sont utilisées (Waters SepPak Porapak RDX (500 mg)). La nitroglycérine (NG) a été choisie comme analyte et elle a été détectée par un système de chromatographie liquide (HPLC) avec détection par double longueur d'onde. Pour une solution de 1 mg/L NG, les résultats ont montré que la rétention diminuait lentement avec l'augmentation du volume de solution passé sur la cartouche : après 2 litres la rétention était supérieure à 96% et après 4 litres, elle était supérieure à 86%.

This page intentionally left blank.

# Table of contents

---

Abstract .....	i
Résumé .....	i
Table of contents .....	iii
List of figures .....	iv
1 Introduction.....	1
2 Experimental.....	2
2.1 Preparation of the NG solution.....	2
2.2 Extraction .....	3
2.3 Sample preparation.....	4
2.4 Analysis .....	4
3 Results and Discussion .....	6
4 Conclusion.....	9
List of symbols/abbreviations/acronyms/initialisms .....	11

## List of figures

---

Figure 1: Extraction setup .....	3
Figure 2: Collection of the effluent in 125 mL Erlenmeyer flasks.....	4
Figure 3: Breakthrough study for NG using the Sep-Pak® Vac 6cc Porapak® cartridges for 2 L solutions (a : full scale, b: enlargement) .....	6
Figure 4: Breakthrough study for NG using the Sep-Pak® Vac 6cc Porapak® cartridges for 4 L solution .....	8

# 1 Introduction

---

The preconcentration of explosive materials from aqueous solutions is necessary for two main reasons. The first and foremost is that most of these samples present low concentrations of explosives such that, if the sample was analyzed as is, the concentration would be under the detection limit of most of the analytical systems. The second is that the analytical techniques such as gas chromatography that is used on a regular basis in laboratories do not allow the direct injection of aqueous solutions.

Once the aqueous sample has been obtained from a well, a pond, a river or any other water source, it is brought back to the laboratory and a 1-L sample is extracted with a cartridge that contains a solid phase that is selective for the analytes of interest. This procedure is known as Solid Phase Extraction (SPE). The experiments described here were aimed at determining if a larger volume can be extracted or if breakthrough happens. Nitroglycerin (NG) was chosen as the analyte.

## 2 Experimental

---

The retention of NG by the Waters, Sep-Pak® Vac 6cc (500mg) Porapak® RDX cartridges (Part # WAT047220, Lot # 003037282A) was tested by extracting 2 and 4-L aliquot of MilliQ water that has been spiked with a concentrated NG solution (known concentration). Samples of the effluent waters were collected at regular intervals in order to determine if NG was present. The analyses were made by High Pressure Liquid Chromatography (HPLC) at Cold Regions Research & Engineering Laboratory (CRREL) (Hanover, NH).

### 2.1 Preparation of the NG solution

The preparation of the 2 L spiked aqueous solution (in duplicate) was carried out by diluting 10 µL of a concentrated solution of NG in acetone (around 205.45 mg/mL) into 2 000 mL of Milli Q water in a volumetric flask. Two solutions were made at the same time and they were mixed together thoroughly in a large clean container to have exactly the same solution for both replicates. The concentrations of the two solutions were confirmed by HPLC before extraction with the cartridge. The concentration of each solution was 1.379 mg/L NG (same concentration in the two flasks).

The preparation of the 4-L aqueous solution of NG solution was made using the very same procedure as described for the 2-L solutions. The concentration determined by HPLC for this new solution is 1.117 mg/L.

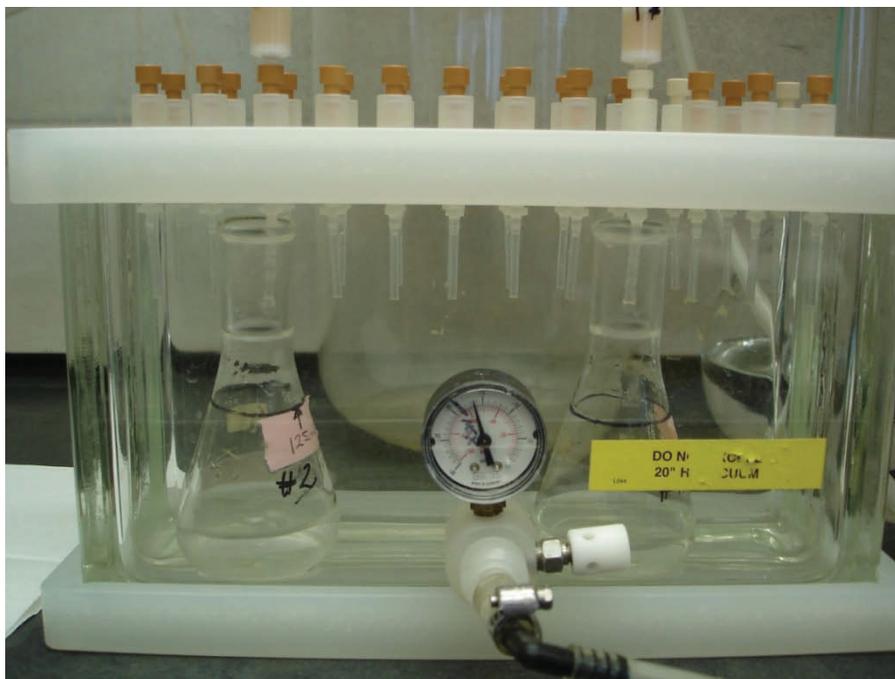
## 2.2 Extraction

The extraction cartridges were labelled, put onto the manifold and conditioned with 15 mL acetonitrile and 30 mL water. The washing solutions were discarded. After the cleaning step, the aqueous NG solution was extracted with the cartridge at rate of 10 mL/min. To collect the effluent, a 125 mL Erlenmeyer flask was placed below each cartridge. The necks of the flasks were long enough so that spitting of the solution outside the flasks did not occur. Glass pipettes (100 mL and 25 mL) were used prior to the beginning of the extraction procedure to identify with precision the position of the liquid level at 125 mL. A clear marking was made and was used throughout the study.

The NG solution in the 2000 mL flasks was delivered to the cartridges using suction lines connected to a vacuum. Picture of the setup can be seen in Figures 1 and 2. The flow of water inside the cartridge was controlled independently for each cartridge. The supply of water to the cartridge was stopped when the volume inside the flasks reached 125 mL. When the two flasks in the manifold had reached 125 mL, the vacuum was removed and an aliquot of each solution (7 mL) was put in an amber vial (7 mL) and kept to be prepared and analyzed. The vacuum was stopped for as little time as possible, to avoid the drying of the cartridges.



*Figure 1: Extraction setup*



*Figure 2: Collection of the effluent in 125 mL Erlenmeyer flasks*

## 2.3 Sample preparation

The solutions were prepared for analysis by mixing 900  $\mu\text{L}$  of the aqueous effluent with 300  $\mu\text{L}$  of acetonitrile. This procedure was necessary so that the samples would have the same matrix as the calibration standards. The 900  $\mu\text{L}$  volume was measured with an automatic pipette (Thermo Labsystems Finnipipette) (tip rinsed with Milli Q water between each solution) and the 300  $\mu\text{L}$  volume of acetonitrile was measured with a glass microliter syringe (Hamilton).

## 2.4 Analysis

The system used for all the HPLC analyses is a Thermo Finnigan Spectra System AS 3000, equipped with a Spectra System UV 2000 dual wavelengths detector (NG detection at 210 nm) and a Spectra System P 4000 solvent delivery system. The eluent is 85:15 water: isopropanol pumped at 1.40 mL/min in the Waters C8 Nova-Pak  $\text{\textcircled{R}}$  4  $\mu\text{m}$  column (3.9 x 150 mm) maintained at 28°C. The solvent is recycled when clean with a Alltech Solvent Recycle Junior. The standard solutions used for calibration were diluted with acetonitrile (3:1, water : ACN), as for the samples. All values presented in the Results

section account for the dilution factor and they reflect the actual concentration in the samples.

The HPLC analysis was done the very same day that the extraction process. Calibration standards were prepared from a solution obtained from Restek (Bellefonte, PA, USA). The calibration at 1.00 mg/L was done at the beginning of the run and continuous calibration verification (CCV) was done every 10 injections, with a previous wash (3:1 water:acetonitrile). The relative standard deviation (RSD) for the CCV was 1.4% for the analysis of the effluents of cartridges #1 and #2.

### 3 Results and Discussion

---

All results are presented as NG retention percentage as a function of the total volume of effluent through the cartridge. Figure 3 presents the results obtained for the extraction of the NG present in the 2-L solution. Figure 3a presents the complete scale (0-100 %) and Figure 3b presents an enlargement. This percentage was obtained by easy calculation using the known concentration in the solution to be extracted in the cartridge and the concentration in the effluent. The retention decreases slowly with the increasing volume, but even after 2 L, the retention was still over 96%. The results show that there is no obvious breakthrough after 2 L of solution was passed through the cartridge. Overall, the average retention for a 2 L volume is 97.6% (duplicates).

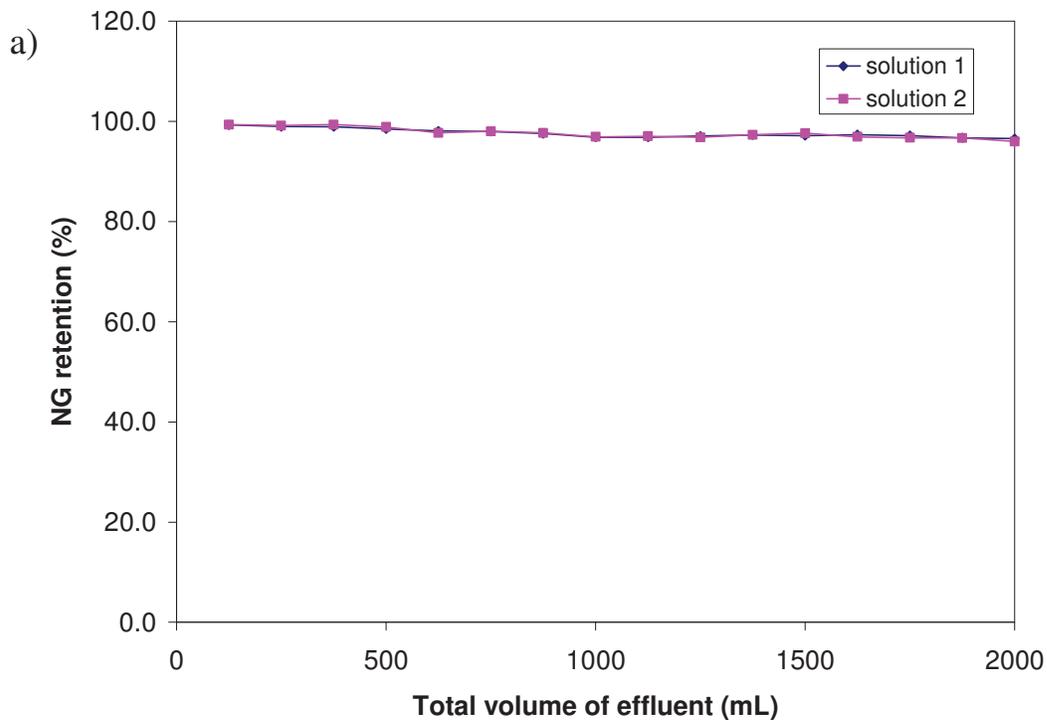


Figure 3: Breakthrough study for NG using the Sep-Pak® Vac 6cc Porapak® cartridges for 2 L solutions (a : full scale, b: enlargement)

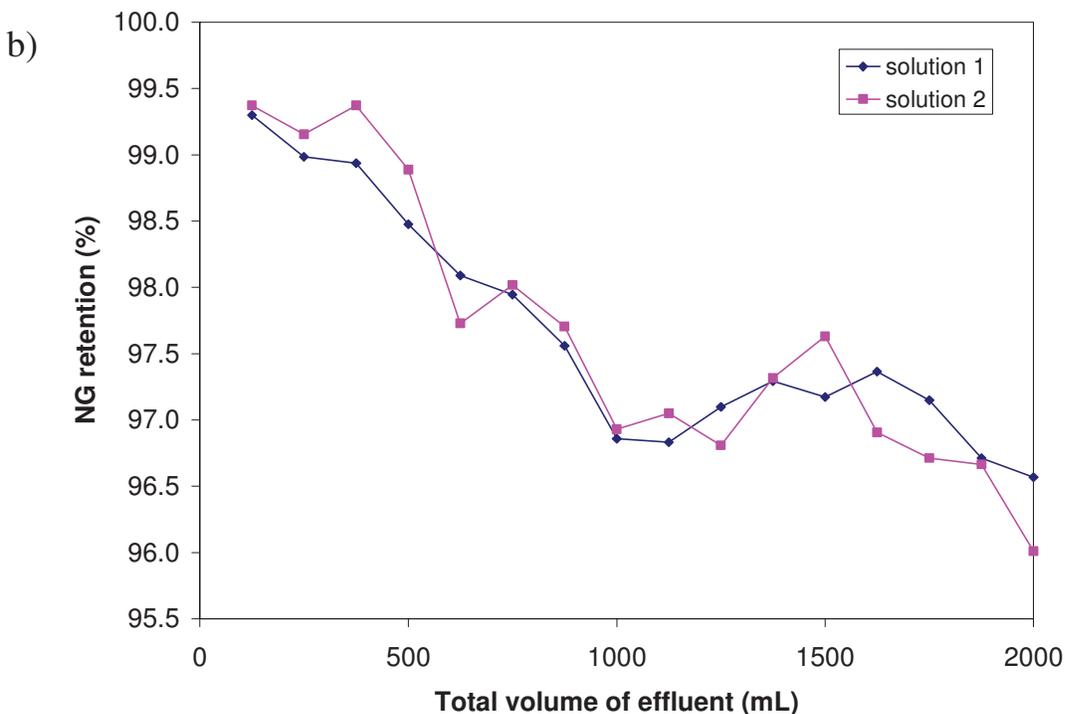


Figure 3 (continued): Breakthrough study for NG using the Sep-Pak<sup>®</sup> Vac 6cc Porapak<sup>®</sup> cartridges for 2 L solutions (a : full scale, b: enlargement)

In order to determine if clear breakthrough occurs at higher volumes, a 4-L aqueous solution of NG solution was extracted in a new cartridge at the same rate and in the same conditions then cartridges for the 2 L solutions. Aliquots were taken every 500 mL from 0 to 1500 mL, and then every 250 mL until all the liquid has been extracted. The RSD for the CCV of these effluents was 2.2%. Results are presented in Figure 4.

The breakthrough was not clearly identified after 4 L of solution. The retention % of NG is still over 86% after 4L. This leads to an average overall retention of 92.5%.

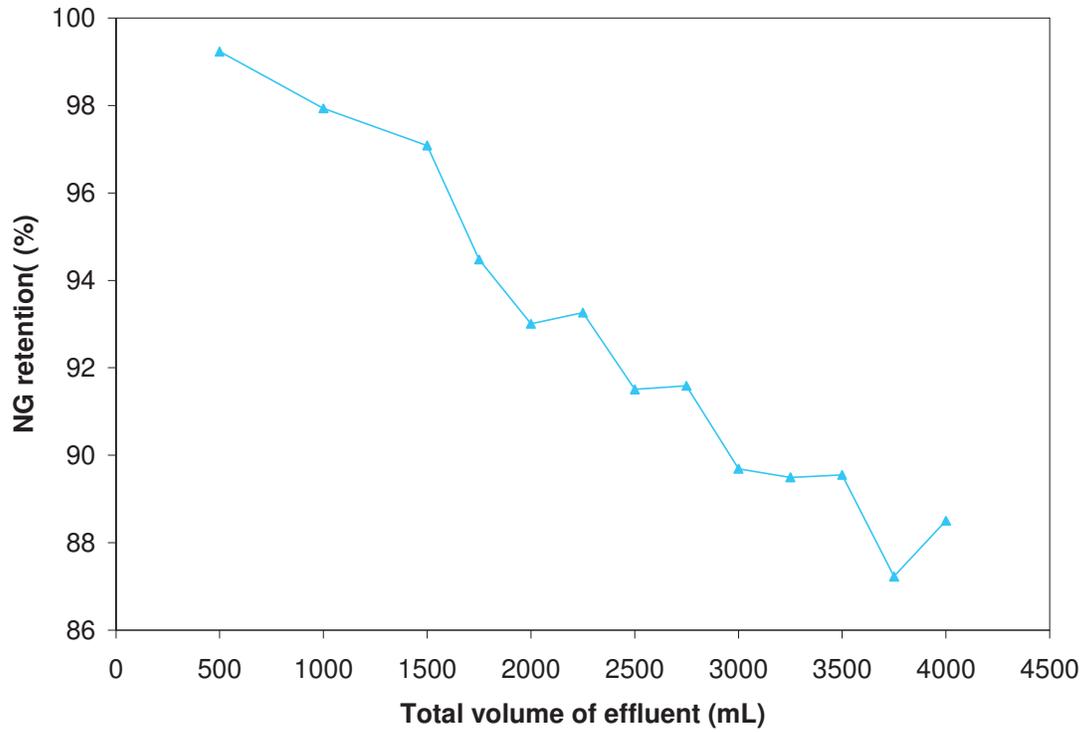


Figure 4: Breakthrough study for NG using the Sep-Pak<sup>®</sup> Vac 6cc Porapak<sup>®</sup> cartridges for 4 L solution

## 4 Conclusion

---

The breakthrough of NG during extraction with the Sep-Pak® Vac 6cc Porapak RDX® cartridges for was not observed after the extraction of 2 L of solution, neither for the extraction of a 4 L solution. The concentration in all solutions to be extracted was over 1 mg/L, which is higher than the majority of the samples collected in the field, but was necessary to obtain effluent concentrations of concentration high enough to be directly analyzable by HPLC in the case of breakthrough.

It would thus be possible to use larger volumes for extraction and thus increase the amount of explosives adsorbed on the resin without leading to breakthrough. This would be helpful for samples with low concentration of explosives or for large samples obtained from multi-increment sampling.

This page intentionally left blank.

## List of symbols/abbreviations/acronyms/initialisms

---

DRDC	Defence Research & Development Canada
ERDC CRREL	Engineer Research and Development Center –Cold Regions Research and Engineering Laboratory
HPLC	High pressure liquid chromatography
NG	Nitroglycerin
L	Liter
%	Percent
SPE	Solid phase extraction
µL	Microliter
mg	Milligram
mL	Milliter
°C	Degree Celcius
mm	Millimeter
CCV	Continuous calibration verification
RSD	Relative standard deviation

This page intentionally left blank.

<b>DOCUMENT CONTROL DATA</b>		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)		
1. ORIGINATOR (The name and address of the organization preparing the document. Organizations for whom the document was prepared, e.g. Centre sponsoring a contractor's report, or tasking agency, are entered in section 8.)  <b>DRDC Valcartier</b>	2. SECURITY CLASSIFICATION (Overall security classification of the document including special warning terms if applicable.)  <b>UNCLASSIFIED            (NON-CONTROLLED GOODS)            DMC A            REVIEW: GCEC JUNE 2010</b>	
3. TITLE (The complete document title as indicated on the title page. Its classification should be indicated by the appropriate abbreviation (S, C or U) in parentheses after the title.)  <b>Breakthrough study for Waters, Sep-Pak® Vac 6cc (500mg) Porapak® RDX cartridges for the retention of nitroglycerin</b>		
4. AUTHORS (last name, followed by initials – ranks, titles, etc. not to be used)  <b>Isabelle Poulin, Marianne Walsh, Alan Dewitt</b>		
5. DATE OF PUBLICATION (Month and year of publication of document.)  <b>November 2011</b>	6a. NO. OF PAGES (Total containing information, including Annexes, Appendices, etc.)  <b>20</b>	6b. NO. OF REFS (Total cited in document.)  <b>0</b>
7. DESCRIPTIVE NOTES (The category of the document, e.g. technical report, technical note or memorandum. If appropriate, enter the type of report, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.)  <b>Technical Note</b>		
8. SPONSORING ACTIVITY (The name of the department project office or laboratory sponsoring the research and development – include address.)  		
9a. PROJECT OR GRANT NO. (If appropriate, the applicable research and development project or grant number under which the document was written. Please specify whether project or grant.)	9b. CONTRACT NO. (If appropriate, the applicable number under which the document was written.)	
10a. ORIGINATOR'S DOCUMENT NUMBER (The official document number by which the document is identified by the originating activity. This number must be unique to this document.)  <b>DRDC TN 2012-073</b>	10b. OTHER DOCUMENT NO(s). (Any other numbers which may be assigned this document either by the originator or by the sponsor.)	
11. DOCUMENT AVAILABILITY (Any limitations on further dissemination of the document, other than those imposed by security classification.)  <b>UNLIMITED</b>		
12. DOCUMENT ANNOUNCEMENT (Any limitation to the bibliographic announcement of this document. This will normally correspond to the Document Availability (11). However, where further distribution (beyond the audience specified in (11) is possible, a wider announcement audience may be selected.)  <b>UNLIMITED</b>		

13. **ABSTRACT** (A brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), (R), or (U). It is not necessary to include here abstracts in both official languages unless the text is bilingual.)

Analysis of water samples from military ranges and training areas as well as from explosive manufacturing plants is common. Water samples can come from groundwater wells, lakes, streams, rivers and ponds. The preconcentration of explosive materials from these aqueous solutions is necessary to allow system compatibility (i.e. some analytical systems can process samples in organic solvent) and to ensure that the concentration are above detection limit. Preconcentrating the sample is done using a Solid Phase Extraction cartridge. The experiments described in this note were aimed at determining if it is possible to extract a volume larger than the common 1L or if breakthrough happens when using the standard cartridge for energetics (Waters SepPak Porapak RDX (500 mg)). Nitroglycerin (NG) was chosen as the analyte and it was analyzed using a liquid chromatography (HPLC) system with dual wavelength detector. For a 1 mg/L NG solution, results show that the retention decreases slowly with the increasing volume processed on the cartridge, after 2 L, the retention of NG was still over 96%, and after 4-L, the retention is still over 86%.

14. **KEYWORDS, DESCRIPTORS or IDENTIFIERS** (Technically meaningful terms or short phrases that characterize a document and could be helpful in cataloguing the document. They should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location may also be included. If possible keywords should be selected from a published thesaurus, e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus identified. If it is not possible to select indexing terms which are Unclassified, the classification of each should be indicated as with the title.)

Nitroglycerin, breakthrough, cartridges, water, samples, preconcentration, HPLC, chromatography, explosive