Application Note

Handheld Chemical Identification

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Direct Determination of the Concentration of Nitric Acid Using Spatially Offset Raman Spectroscopy

Implementation of a nitric acid library with the Agilent Resolve Raman and Command software

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Abstract

Acids, such as nitric acid, are typically available in a variety of strengths, concentrations, and levels of purity. Nitric acid is a common strong mineral acid and a powerful oxidizing agent that has many industrial, laboratory, and commercial uses. Depending on its concentration, nitric acid ranges from a low to highly hazardous material.

Raman spectroscopy can identify variations in the spectra of nitric acid based on its concentration. To create a library for the Agilent Resolve handheld Raman analyzer, a set of eight nitric acid samples of different concentrations were analyzed in glass vials in Spatially Offset Raman Spectroscopy (SORS) mode. Agilent Resolve Command centralized system management software was used to create a user spectral reference library for nitric acid. The library, which was created on a PC, was then deployed to the portable Resolve analyzer for testing. The study shows the effectiveness of the method for identifying nitric acid at 32.5, 65, and 95%. The ability to positively discriminate the various samples of nitric acid directly, *in situ*, enables laboratories to quickly assess the risk of an acid based on its concentration.

Introduction

Nitric acid is a strong mineral acid that is widely used both as a laboratory reagent and in many industrial processes. It is a strong acid, meaning that it dissociates completely in water, and an oxidizing agent, as it can readily donate oxygen atoms and accept electrons in reactions. As a powerful oxidizing agent, concentrated nitric acid can react explosively with non-metallics, releasing huge amounts of energy. It is also used extensively as a nitration agent, readily donating a nitro group, typically to an organic molecule.[1]

As outlined in Table 1, the hazards associated with nitric acid are proportional to the concentration of the acid. At 10 M or above, the acid is both corrosive and oxidizing, and therefore particularly dangerous. While dilute nitric acid of less than 0.1 M is not classed as hazardous, it can still cause harm to eyes and skin, so should be handled with care. The CAS registry number for nitric acid is 7697-37-2, regardless of the concentration—or hazard—of the acid.

The changing concentration of nitric acid leads to distinct changes in the Raman spectra. As the spectral changes are directly related to the types of chemical species present in the acid, Raman spectroscopy has been used to check the concentration of nitric acid on benchtop systems. In this application note, a handheld through-barrier technique is reported.

The Agilent Resolve Handheld Raman Analyzer was used to acquire the Raman spectra of a series of nitric acid samples with different concentrations. The Agilent Command Fleet Management Software was then used to create a user spectral reference library for nitric acid. The library was deployed to the portable Resolve analyzer for testing, using the Spatially Offset Raman Spectroscopy (SORS) through-barrier mode. SORS allows users to quickly identify the concentration and hazard status of an unknown nitric acid sample in its container, ensuring the safety of the operator.

Table 1. Hazard classifications of different concentrations (molarity) of nitric acid.

Nitric Acid Concentration	GHS* Hazard Label	Notes
<0.1 M (0.4%)	Not classified	Care is needed when handling dilute nitric acid, as it may cause harm to eyes and skin.
0.1 to 0.8 M	 Irritant	Irritating to eyes and skin.
0.8 M (3%) to 10 M	 Corrosive	Can cause severe burns and damage to eyes.
>10 M (45%)	 Corrosive and oxidizing	Concentrated nitric acid is a fire risk, causes severe burns, skin staining, and peeling, and produces toxic fumes. Safety precautions and proper handling procedures are needed when working with hazardous substances.
15.25 M (68%), lab grade concentrated acid		
19.28 M (86%), red fuming nitric acid		
>21.3 M (95%), white fuming nitric acid		

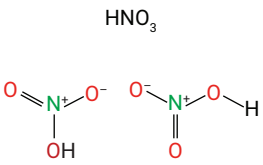
*Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Experimental

Samples

A new bottle of 98% nitric acid (98% HNO_3, 21.98 M, pH −1.34) was diluted using de-ionized water to create the range of acid samples shown in Figure 1. The solutions were stored in enclosed clear glass jars in preparation for analysis by the Resolve handheld Raman analyzer in SORS through-barrier mode.

A verification set of nitric acid samples at 32.5, 65, and 95% was also prepared. To provide a more rigorous test for the SORS technique, the solutions were decanted into amber glass bottles.



% HNO_3	M
98%	21.98
88%	19.73
78%	17.49
68%	15.25
58%	13.01
48%	10.76
38%	8.522
28%	6.279

Figure 1. Chemical structure of nitric acid (left) and concentration in %HNO_3 by volume and molarity denoted by M of the standards analyzed in this study (right).

Instrumentation

The Resolve handheld Raman analyzer was used with standard (default) acquisition settings and full laser power in the SORS through-barrier mode.

Library generation

After data collection, the database of scanned samples was exported onto a PC via a USB memory stick. The Agilent Resolve Command centralized system management software was used to open the file and create a custom library for nitric acid based on the spectral data and metadata. The software created a custom nitric acid Command library file that was then sent to the Resolve handheld Raman analyzer. The main steps involved in the generation and deployment of a user library are shown in Figure 2.

Once the new library (named as "Nitric dilutions") was installed onto the Raman Resolve analyzer, it was checked to ensure that the correct spectra and metadata had been added, as shown in Figure 3.

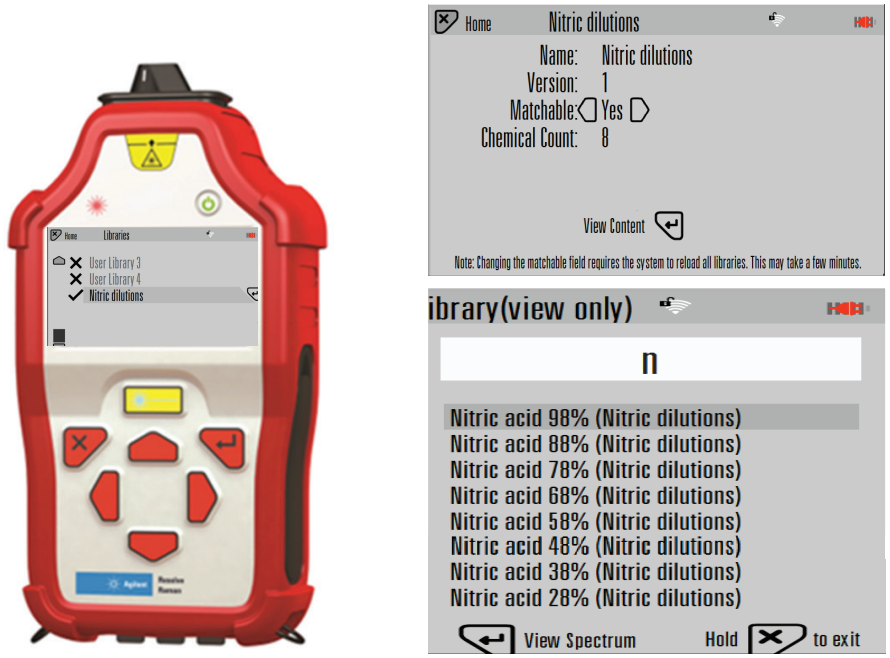


Figure 3. Agilent Resolve handheld Raman analyzer screenshots showing the details of the newly created "Nitric dilutions" library.

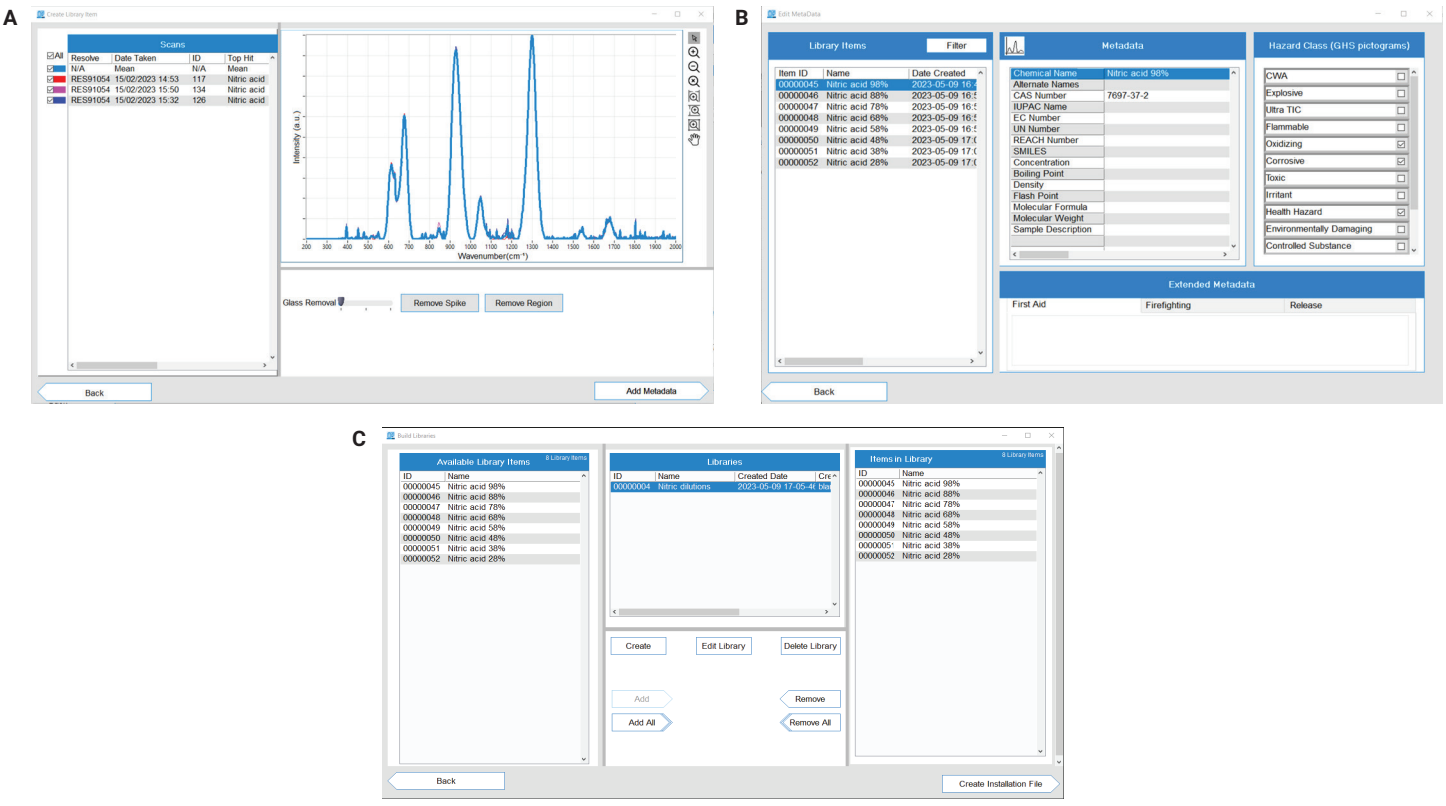


Figure 2. Selected Agilent Resolve Command software screenshots of the library-creation process. (A) Create a library item for each concentration. (B) Add metadata and hazard class for each library item. Repeat until all items are complete. (C) Add the desired library items to the new library and then create an installation file for deployment to the Agilent Resolve handheld Raman analyzer.

Results and discussion

Eight nitric acid samples of different concentrations (detailed in Figure 1) were analyzed using the Resolve handheld Raman analyzer in SORS through-barrier mode. The Raman spectra were collected for each of the dilutions reported in Figure 1 and are plotted in Figure 4.

Figure 4 shows clear changes in the spectra from the most concentrated acid to the more dilute samples, as the water content changes. These spectra were used to create the Resolve matching library for nitric acid, as described in Figure 2 and the workflow that is outlined in Figure 5.

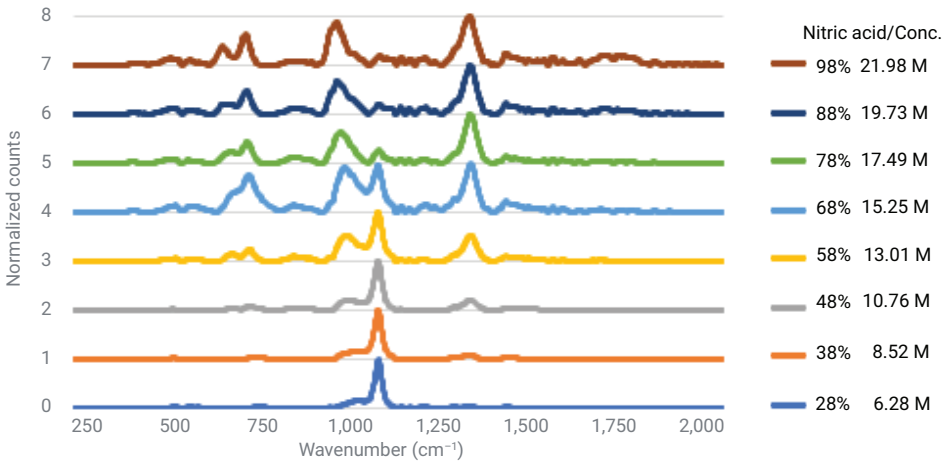


Figure 4. Normalized Agilent handheld Raman analyzer SORS spectra for nitric acid at different concentrations, ranging from (top) highly concentrated (98%, most concentrated) to lowest measured concentration (28%, bottom of figure). Any solution of nitric acid greater than 86% is termed "fuming", where the acid reacts directly with air. Extra care must be taken when handling fuming nitric acid.

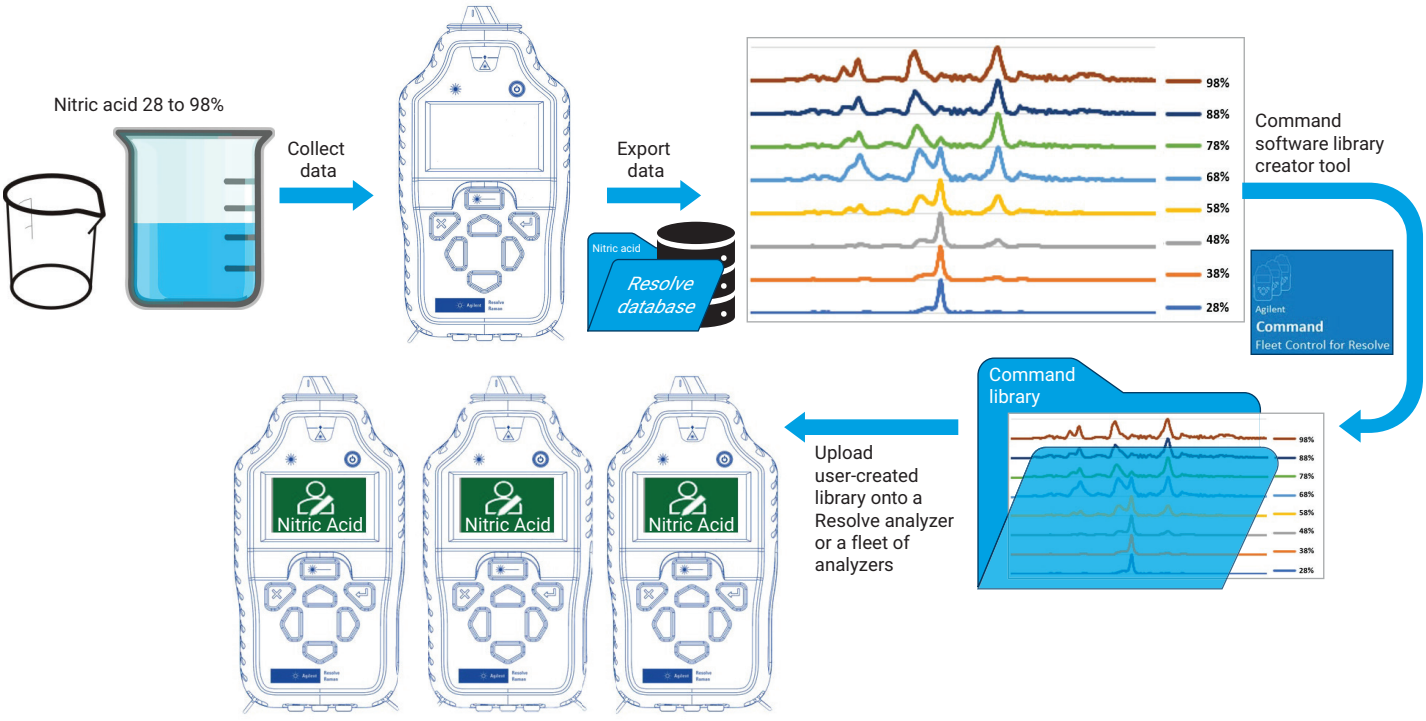


Figure 5. Workflow of data collection, library creation, and uploading of the user-created nitric acid library from Agilent Resolve Command software to one or a fleet of Agilent Resolve handheld Raman analyzers.

To check the validity of the library, the three verification samples of nitric acid were measured as "unknowns" by the Resolve analyzer. As shown in Figure 6, the spectra of the three test samples were compared to the reference spectra in the "Nitric dilutions" library. Good matches were achieved between each test solution (32.5, 65, and 95%) in amber glass bottles and the library spectra of acids with the closest concentration (28, 68, and 98%). As the water content of nitric acid increases, the degree of acid dissociation and chemical species present in the binary water and acid mixture changes. Despite these variations, the match quality remained high (above 90%) for the three acid concentrations.

Conclusion

The study has shown the effectiveness of the Agilent Resolve handheld Raman analyzer in SORS through-barrier mode for the determination of the concentration of unknown samples of nitric acid. All samples were analyzed directly in containers using the portable system, protecting the user from exposure to potentially hazardous materials.

Agilent Command fleet management software was used to create a reference library based on the Resolve spectra of a series of concentrations of nitric acid. Once the "Nitric dilutions" library had been exported back to the Resolve, it provided good match data for three verification samples with concentrations near but not the same as in the library.

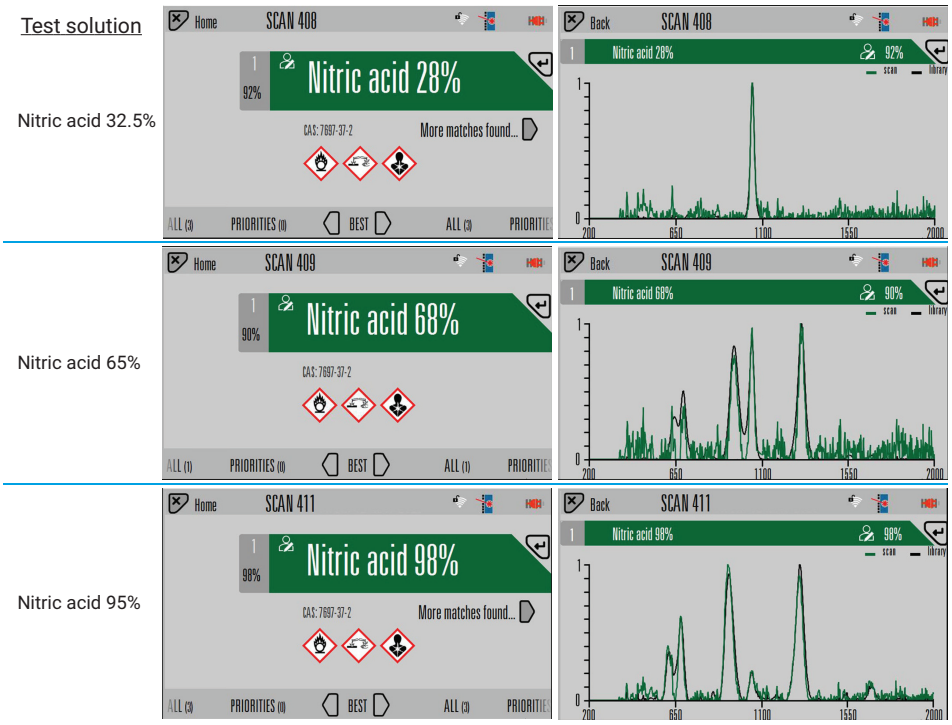


Figure 6. Match value and the spectral overlay of the three verification samples of nitric acid at 32.5, 65, and 95% (green traces) with the reference spectra in the Agilent Resolve system's "Nitric dilutions" library (black trace).

The ability to discriminate and approximately quantify nitric acid at 32.5, 65, and 95% using a fast, direct, and simple SORS method is useful for user-safety, since the hazard-level of the acid is directly proportional to its concentration.

The addition of the Command software capability to the powerful spectroscopic performance of the Resolve analyzer provides users with the flexibility to create, manage, and distribute custom Raman libraries for other reagents.

Reference

1. Greenwood, N. N., Earnshaw, A. Chemistry of the Elements (2nd ed.). *Butterworth-Heinemann* **1997**, 465–471. ISBN 978-0-08-037941-8.

Further information

Resolve Handheld Raman Analyzer

Command Fleet Management Software

Resolve Handheld Raman Analyzer FAQs

Raman Spectroscopy FAQs

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