The 5975 inert MSD – Benefits of Enhancements in Chemical Ionization Operation

Technical Note

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Abstract

The full power of chemical ionization (CI) mass spectrometry (MS) is now conveniently available through the complete integration of CI on the 5975 inert MSD (mass selective detector). CI has been fully automated by providing auto-tuning with electronic control of the reagent gases. All modes of MS operation in a single sequence, completely free of operator intervention, are now possible. Analytes can be sensitively determined in samples by implementing alternating positive- or negative-CI (PCI or NCI) modes. On the 5975 inert MSD, CI is as easy as EI (electron impact ionization).

Introduction

CI lends selectivity and specificity to the ionization process and is a powerful tool in MS. As an alternative approach to EI ionization, CI can provide enhanced analyte detection in complicated matrices or assistance in confirmation of compound identity. In most cases, based on the particulars of the compounds of interest, a choice between PCI and NCI modes can be made and optimized. This optimization requires selecting an appropriate reagent gas and exploring the various parameters such as source temperature, reagent pressure or flow, etc., to obtain the desired performance. This has been a manual process in the past but with the new integrated electronic control of the CI gases available in the 5975 inert MSD, many of these tasks can be automated. In some cases the analytical situation is not clear-cut and samples contain analytes that require acquisition in PCI and NCI modes. Because the parameters that optimize these two modes of performance are often very different, manual implementation of the appropriate methods was the rule. Again, integration of CI control makes it possible to alternate modes without compromising the important method parameters.

The new CI control provides –

- Automated EI ionization tuning of the CI source allowing EI spectra to be acquired in series with CI
- Completely electronic control of the CI gas flow
- Electronic selection of one of two possible CI reagent gases
- Method optimization by survey of reagent flow

Most importantly, this allows the user to perform EI, PCI, and NCI acquisitions within a sequence by alternating between methods. This technical note provides examples of some important features in the enhanced CI control of the 5975 inert MSD.

CI Instrument Interface Enhancements

CI Reagent Control

Figure 1 shows the new CI control panel that replaces the knob and buttons of the 5973N mass-flow controller (MFC). The gas flow setting is still as the percent of the maximum 5 mL/min flow of the MFC. This panel is accessible from the TUNE View and from the Instrument Control View (under CI Controls or by selecting Edit Mass Parameters). Control of the gas flow is provided as well as selection between the A and B channels. The "Shutoff" turns all gases off. Note that changes to the CI gas flow and other tune parameters are saved with a TUNE file and this file must be associated with a method to be executed.

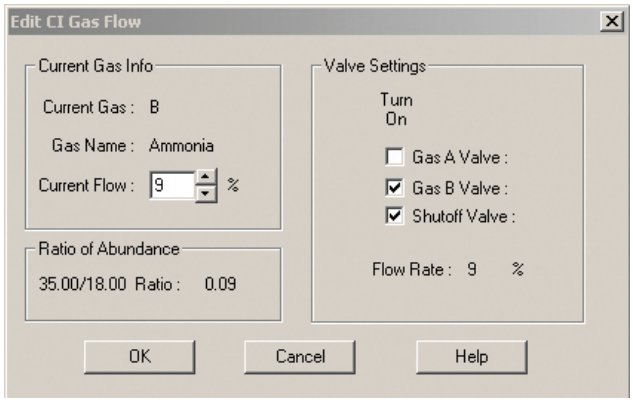

Figure 1. The new CI control panel.

EI tuning of CI source

A menu command automatically executes tuning of the CI source for EI operation, Figure 2. This tuning procedure, like all CI tuning, requires that methane be connected to the instrument at channel A.

Automated CI tuning

In both modes of CI operation, the CI TUNE WIZARD assists the user in configuring the reagent or buffer gas, selecting reagent ions and their ratios, and the tuning ions of the CI tuning gas itself, perfluorodimethyltrioxadodecane (PFDTD). As previously, PCI tuning with PFDTD is available only in methane, and in NCI, both methane and ammonia use the PFDTD tuning compound.

PCI tuning

Previously the user manually adjusted the methane CI gas flow to obtain the proper reagent ion ratios for PCI tuning. This is now automated in both methane and ammonia PCI tunes. After flow adjustment, a PCI Autotune can be executed from the pull down menu.

Additionally, a survey can be conducted of the reagent ion ratios as a function of reagent flow. This allows the user to select various reagent ion ratios to meet specific PCI criteria.

NCI tuning

Methane and ammonia NCI tuning are fully automated, and the 5975 inert MSD software sets default buffer gas flows for tuning for both gases as an initial tune.

Application Examples

In developing CI methods for a known list of compounds, the recommended procedure is quite straightforward. Develop a suitable GC method in EI, then switch to CI and acquire a standard in the various CI modes. Figure 3 shows an example for the sequence table for such a survey. When a particular mode provides the "best" analysis, optimize that mode. The criteria for what is the "best" may be most favorable spectra, or greatest response, or it may include issues concerning the sample matrix, such as minimizing mass spectral interferences.

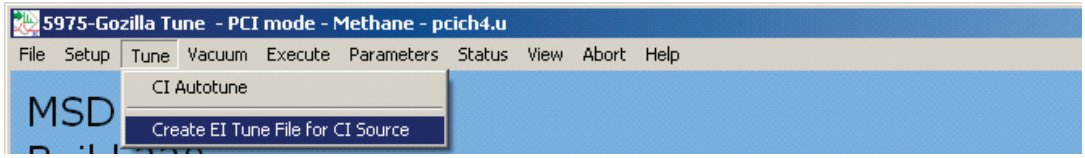

Figure 2. EI tuning of CI source.

Sample Log Table

Data Path: C:\msdchem\1\DATA Browse... Method Path: C:\msdchem\1\METHODS Browse...

	Type	Vial	Sample	Method / Keyword	Data File	Comment / KeywordString
1	Sample	1	Sample or Standard	EI-CIsource	EI-data	EI with CI source
2	Sample	1	Sample or Standard	PCI-Methane	PCICH4-data	PCI CH4 tuned to 20%
3	Sample	1	Sample or Standard	PCI-ammonia	PCINH3-data	PCI NH3 tuned to 10%
4	Sample	1	Sample or Standard	NCI-methane	NCICH4-data	NCI CH4 tuned to 40%
5	Sample	1	Sample or Standard	NCI-ammonia	NCINH3-data	NCI NH3 tuned to 20%
6						
7						

Sheet1

OK Cancel Help

Figure 3. Example of CI survey sequence.

Figure 4 shows the reconstructed total ion chromatogram (RTIC) for one of several phthalates acquired in the two CI modes with two reagent gases. As expected, the spectra in each mode are all different. For these compounds, PCI with ammonia reagent gas provides the greatest response in full scan and the most distinctive spectrum.

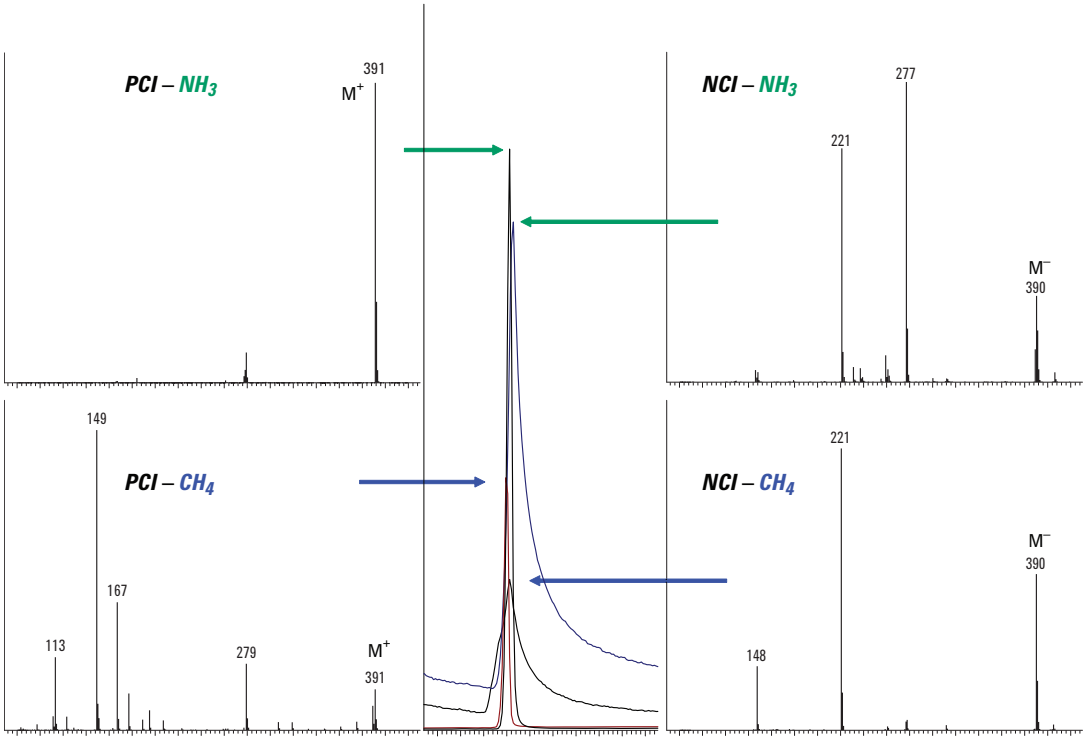

Figure 4. RTIC in PCI and NCI with methane and ammonia CI gases (middle panel) of a dioctyl phthalate. Note the differing spectra and total responses indicated by the arrows.

In Figure 4, the temperature of the source had a profound effect on response and especially chromatographic peak shape. This is most pronounced in NCI mode.

Figure 5 shows an example of optimizing source temperature for the higher molecular weight brominated diphenyl ethers (BDE). Typically NCI favors lower source temperatures but in this case the loss in sensitivity is offset by improved chromatography achieved by the better volatilization of the analytes at higher source temperatures. This data was produced by a sequence where the four methods were the same except for the NCI tune files which had different source temperatures.

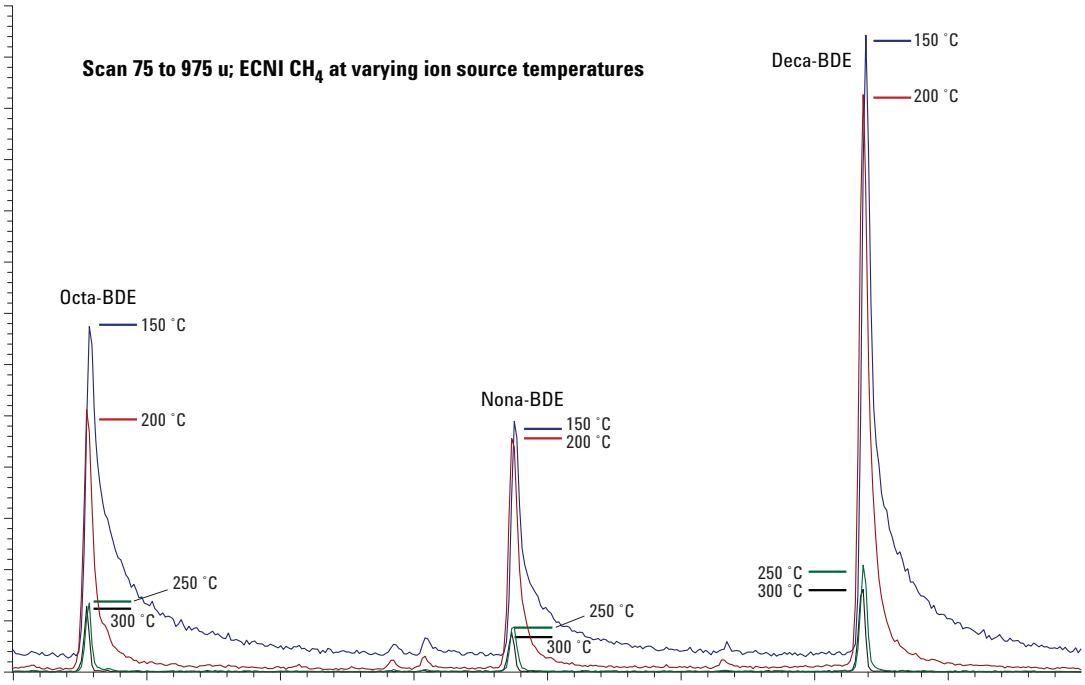

Figure 5. Effect of optimizing NCI source temperature.

CI reagent flow is especially important. In a continuation of the polybrominated diphenyl ethers example, Figure 6 shows the dramatic influence of buffer gas flow into the source. In PCI mode with ammonia reagent gas, this is especially important as ammonia source pressure has a profound effect on the ratio of protonated species ($[M+H]^+$) to the adduct species ($[M+NH_4]^+$) of the analyte molecule ([M]).

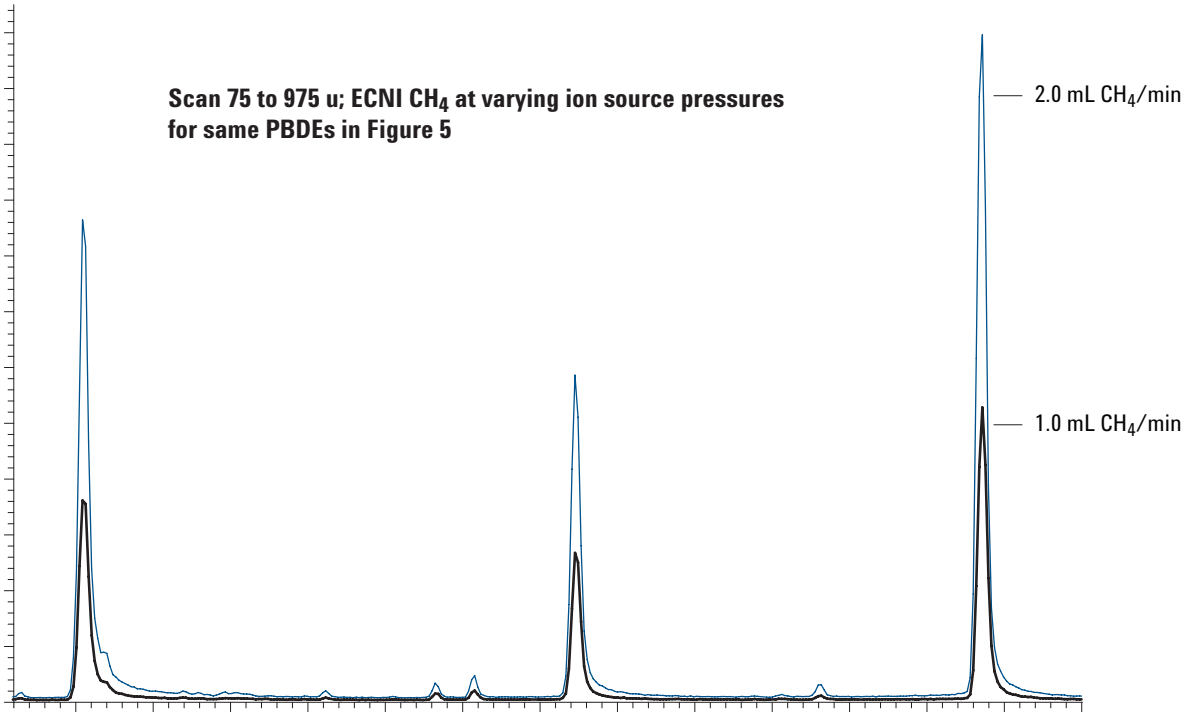

Figure 6. Influence of source pressure on NCI response.

Figure 7 presents such data for the benzophenone PCI checkout compound. Using the reagent ion ratios allows the user to optimize the ratio of the target and qualifying ion for their analysis and to reproduce the results in future tunes. A convenient way to gain this information is through the FLOW SURVEY menu item in CI tune. This feature steps the reagent flow over a user selectable range and presents the results for the response and ratio of responses for two reagent gas ions. It is knowledge of this ratio that is key to optimizing and reproducing PCI performance.

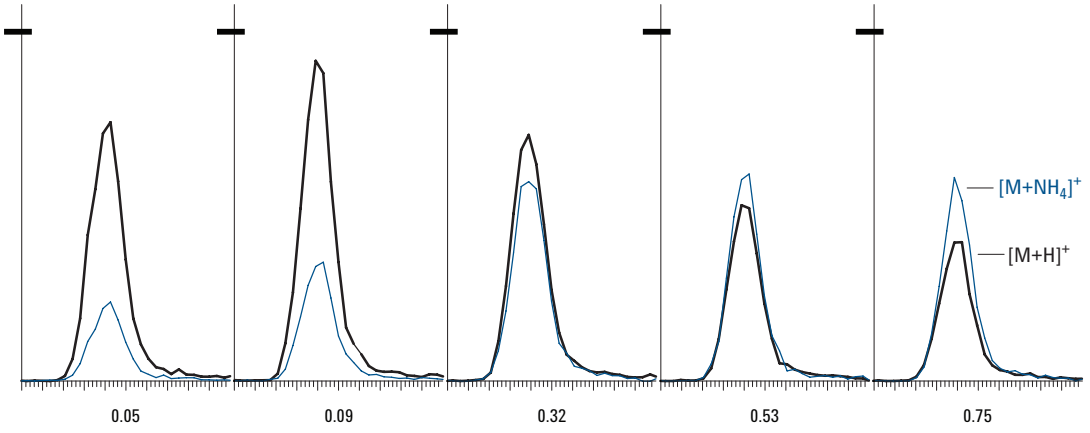

Figure 7. PCI with ammonia reagent gas. Influence of source pressure on benzophenone spectrum as a function of source species seen in the ratio of *m/z* 35 : *m/z* 18.

A convenient way of conducting a series of flow experiments is by employing the command “set-flow #” in a sequence, where “#” represents the setting of the reagent MFC. See Figure 8. This allows a single CI method to be used with different reagent gas flows in a sequence. Similarly, the ability to shutoff the CI gas at the end of a sequence is given by the sequence commands CIGASOFF and PAUSE, Figure 8.

Conclusions

The full power of CI/MS is conveniently available for the analyst through the complete integration of CI on the 5975 inert MSD. CI has been fully automated by providing auto-tuning with electronic control of the reagent gases. Now all modes of mass spectrometric operation in a single sequence that is completely free of operator intervention is possible. This allows analytes to be sensitively determined in samples by implementing alternating PCI or NCI modes. On the 5975 inert MSD, CI is as easy as EI.

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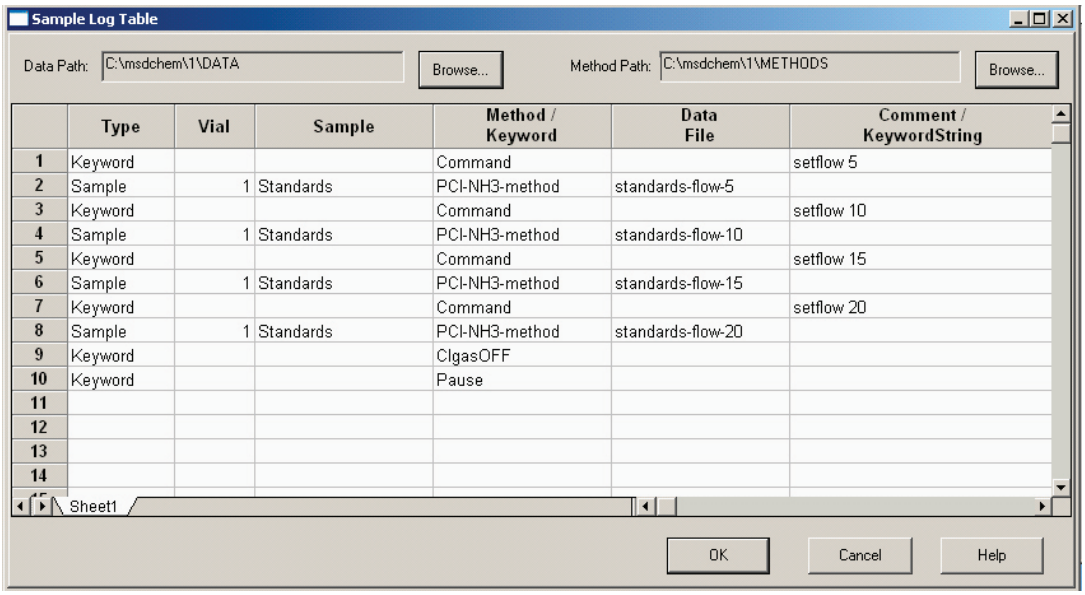

	Type	Vial	Sample	Method / Keyword	Data File	Comment / KeywordString
1	Keyword			Command		setflow 5
2	Sample	1	Standards	PCI-NH3-method	standards-flow-5	
3	Keyword			Command		setflow 10
4	Sample	1	Standards	PCI-NH3-method	standards-flow-10	
5	Keyword			Command		setflow 15
6	Sample	1	Standards	PCI-NH3-method	standards-flow-15	
7	Keyword			Command		setflow 20
8	Sample	1	Standards	PCI-NH3-method	standards-flow-20	
9	Keyword			ClgasOFF		
10	Keyword			Pause		
11						
12						
13						
14						

Figure 8. Commands for changing and shutting off CI gas flow in a sequence.

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