

## Introduction

The technology for easy, direct automated elemental analysis of material retained on certain membranes used in water filtration and air monitoring applications is now available on the Exeter Analytical Model CE440 Elemental Analyzer. Greatest efficiency is achieved using the CE440 equipped with a multi-sample injector, but the technique is also applicable to instruments with single sample automation. The method requires a minimum of sample preparation and only minor alterations in standard instrument operating procedures.

Direct determination of total CHN retained on a filter is more sensitive, precise and cost-effective than making measurements on pre- and post- filtered samples and calculating the difference. This has been confirmed in a study conducted for the EPA on particulate concentrations in water samples from the Chesapeake Bay Monitoring Program (1). Direct determination is preferred over the traditional "by difference" method because of the formers reduced sources of error, rapidity of analysis and increased sample representativeness due to the greater volume filtered.

The advantages of the Exeter Analytical CE440 versus other elemental analyzers lie primarily in its horizontal combustion train which prevents clogging from accumulation of filter and sample ash and its capacity to process filters up to 47 mm in diameter in one analytical cycle. A 7x5 mm nickel sleeves (P/N 6703-0499) is used to contain a filter up to 25 mm or half of a larger filter. For the latter, two sleeves are inserted simultaneously to produce one complete analysis.

## Filters

This technique applies equally to glass or quartz microfiber filters, the choice depending on the particular application. However, to maintain a low, consistent blank value, only the highest quality filter without binder should be used (Whatman 934-AH or GF series of glass fiber filters, Ultra-Pure QM-A quartz filters, or equivalent).

Low cost glass fiber filters of various pore sizes and dimensions are the most common type for collecting particulates in water or air. Smaller filters are preferred when excessive suspended particulates are absent; the advantage is a reduced blank signal and the entire filter can fit into one sleeve. Although glass fiber filters can withstand temperatures up to 550°C, to minimize crumbling and shrinkage it is best to precombust them at a maximum of 450-500°C for up to 16 hours. Nickel sleeves are required during analysis to contain the melt and to prevent spattering during the combustion. The static combustion feature combined with 980°C temperature of the CE440 ensures that no material is entrapped in the melt.

Quartz fiber filters are used in specialized applications, such as flue stack monitoring, because they withstand temperatures up to 1000°C and have increased chemical resistance. For best results, quartz filters should be muffled overnight at 500°C prior to use. They are easy to handle and will remain intact during analysis.

Silver membrane filters, which are completely solvent resistant, should also be compatible with this elemental analysis technique.

### Sample Preparation

#### A. Sampling Procedure

A protocol appropriate for the particular water filtration or air monitoring application should be selected, taking particular care to ensure sample homogeneity and representativeness. Sampling is the single largest determinant of data quality, as the magnitude of variability from handling and analysis is comparatively small. Duplicate, or even triplicate sampling is recommended. Filter blanks should be treated the same as filter samples in all respects except for actual sample collection.

For extra large filters, such as those used in high volume air monitoring, the filter paper should be folded with exposed surface inside and a standard diameter portion excised. The resulting two aliquots should be dried prior to loading for analysis.

A typical method for filtering aqueous solutions is as follows:

1. Place the correct size pre combusted filter pad in a vacuum filtration assembly.
2. Agitate a known volume of water (usually 100 ml) vigorously and quickly pour the sample into the filtration assembly. Another 100 ml of de ionized water can be used to wash through the system. If a wash is used, do the same for the filter blank.
3. Filter at 15 in Hg vacuum to dryness and break the seal.
4. The filter can be optionally vacuum desiccated overnight, folded in half (exposed surface inside), wrapped in aluminum foil or placed individually in a covered petrie dish, labeled and frozen at -10°C for later analysis.
5. Prior to actual analysis, non-desiccated samples or those that have collected condensation should be placed in a drying oven at 45°C overnight.

## B. Filter Preparation for Analysis

Depending on filter size, some variation of the following general approach using the Exeter Analytical HA Filter Kit (P/N 125-00020) is recommended for packing the filter into a 7x5mm nickel sleeve:

1. Work on a non-contaminating surface (e.g. tape aluminum foil that has been muffled at 500°C for one hour onto a work bench).
2. Using two pair of clean forceps (not included in kit), fold the 25 mm filter in half so that the exposed surface is inside. Cut 30-47 mm diameter filters in half, fold each half separately and proceed.
3. Continue folding the filter down from both dimensions until you have a compact package. Compress further with the forceps.
4. Place a 7x5 mm nickel sleeve into the filter loading die, which functions as a holding device.
5. Use the 4 mm loading plunger to force the compressed filter through the Pyrex loading funnel and into the nickel sleeve. For all glass fiber filters and other filters that have heavily loaded with material, we recommend that a small square of muffled aluminum foil be loaded through the funnel into the nickel sleeve before the filter is added. This helps contain possible spatter and loose material.
6. Make sure no excess filter protrudes above the lip of the sleeve.
7. For larger filters, repeat this procedure for each half. The two halves, in separate sleeves, compose one sample for analysis.

## Instrument Operation

Once the filters are packed into the nickel sleeves they can be transferred into the 64 sample wheel. The calibration series must be placed at the beginning of the wheel. This normally consists of a conditioner, a blank, a conditioner and three standards. Normally, OAS grade acetanilide is used to calibrate the instrument. For low level samples you may choose to use a standard that more closely resembles the samples or use a smaller amount (as low as 500.0 ug) of acetanilide. Another option is to use the 'Expanded Read' and 'Expanded Reporting' parameter choices. A standard should also be placed at the end of the wheel and a filter blank should follow each series of ten samples.

By entering 100 for the weight of the filter samples, unitless results are printed out which represent micrograms of C, H and N per filter. This corresponds directly to the known amount of liquid or air that has passed through the filter. The maximum sample capacity per run is approximately 4,000 to 5,000 micrograms of carbon. Filters containing more than that amount (i.e., they appear very dark) can be cut in half and analyzed separately and the results added. For particulate samples collected from water, the hydrogen result is meaningless.

If you are running large filters that require double drop operation, you must put a double drop blank (i.e. - two sleeves) immediately after the standard and use the "Automatic Ks and Blanks" option in order for the correct blank value to be used. For samples or blanks that require the double drop option to occur, you must preface the sample ID with a plus sign (+). Refer to section 4.A in the CE440 manual for more detail.)

### Quality Assurance

Filter blank values should be only slightly higher than the normal instrument blank level; a 0 to 5 uV increase in Nitrogen and up to 100 uV increase in Carbon are typical. Large filters will show more variability in their blank values. Greater increases or high variability indicate poor quality filter pads or a problem in sample/blank preparation technique.

Precision of sample duplicates is generally lower than typical organic standards due primarily to the variability in sampling. However, greater than 15 to 20% variation may indicate an error beyond a sampling problem. Samples containing different particle sizes should be run in triplicate. One recommended procedure is to spike some filters with a known quantity of material and look for good recovery.

### Other Applications

The technique described above is limited to total C, H and N. A number of alternatives to analyze for organic, inorganic or free carbon have been proposed, but there is no standard method available to date.

- (1) D'Elia, C.F. et al "Nitrogen and Phosphorus Determinations in Estuarine Waters: A Comparison of Methods Used in Chesapeake Bay Monitoring", Report prepared for Chesapeake Bay Program Liaison Office, Region III, US EPA, Annapolis, MD. 1987.