



NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

**EVALUATION OF
ANALYTICAL APPROACHES FOR THE
MEASUREMENT OF FORMALDEHYDE
IN PULP MILL TREATED EFFLUENTS**

SPECIAL REPORT NO. 07-03

APRIL 2007

**by
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Acknowledgments

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PRESIDENT'S NOTE

A longstanding cornerstone of NCASI's Technical Studies Program is the development and validation of analytical testing procedures suitable for support of research or regulatory uses. Based on past experiences and exploratory work, it was determined that evaluation of the formaldehyde methods specified in the Quebec *attestations d'assainissement* industrial effluent permit testing program was warranted. This report summarizes the results of evaluations of the two methods specified for use in that program. The results demonstrate the need for careful and thorough evaluation of test procedures used to support regulatory decisions to ensure that unbiased methods are employed. Rote implementation of the procedures was found to introduce a significant positive bias through the interaction of some effluent constituents and the pentafluorobenzylhydroxylamine (PFBHA) derivatization chemistry employed by both subject methods. This unique interaction caused conversion of methanol to formaldehyde, thus producing a result that was not at all representative of the effluent being tested. This report explores the applicability of these findings to different sources of effluent and potential means of mitigating the bias through use of antioxidants. Partial solutions are offered, and the report makes it clear that utilization of PFBHA chemistry for the analysis of formaldehyde in pulp mill effluents can only be justified if there is a concurrent demonstration of the absence of any residual methanol in the effluent. This important finding and other outstanding analytical method performance questions identified herein will be of significance in the guidance of any future formaldehyde effluent monitoring studies.

A handwritten signature in black ink, appearing to read "Ron Yeske", is positioned above the printed name.

Ronald A. Yeske

April 2007

MOT DU PRÉSIDENT

Le développement et la validation des procédures analytiques soutenant la réglementation ou les activités de recherche constituent, depuis longtemps, la pierre angulaire du Programme d'études techniques de NCASI. Selon les expériences passées et les travaux exploratoires, les chercheurs ont déterminé que l'évaluation des méthodes de caractérisation du formaldéhyde spécifiées dans le programme québécois d'attestation d'assainissement en milieu industriel était justifiée. Ce rapport fait la synthèse des résultats de l'évaluation des deux méthodes retrouvées dans le programme. La synthèse démontre bien la nécessité d'évaluer soigneusement et de façon exhaustive les procédures sous-jacentes aux décisions réglementaires afin de s'assurer que des méthodes non biaisées sont utilisées. Les auteurs ont déduit que l'application machinale des procédures en question génère un important biais positif suite à l'interaction de certains constituants de l'effluent avec les produits de dérivation effectuée à l'aide de *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) dans chacune de ces méthodes. Cette interaction inattendue a causé la conversion du méthanol en formaldéhyde, ce qui a généré un résultat aucunement représentatif de l'effluent analysé. Le rapport explore l'application possible de ces observations à différentes sources d'effluents et les moyens éventuels pour mitiger le biais en utilisant des agents antioxydants. Les auteurs offrent des solutions partielles et le rapport spécifie que l'utilisation des dérivés du PFBHA pour l'analyse du formaldéhyde dans les effluents de fabriques de pâtes est valide seulement si l'absence de méthanol résiduel dans l'effluent est démontrée. Cet important résultat, de même que les autres questions essentielles portant sur la performance des méthodes analytiques identifiées dans ce rapport, demeureront significatifs pour orienter les prochaines études sur le suivi du formaldéhyde dans les effluents.



Ronald A. Yeske

Avril 2007

EVALUATION OF ANALYTICAL APPROACHES FOR THE MEASUREMENT OF FORMALDEHYDE IN PULP MILL TREATED EFFLUENTS

SPECIAL REPORT NO. 07-03
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ABSTRACT

Quebec mills were instructed to have effluent samples tested for formaldehyde using either Standard Method 6252B or MA 403–SP.O₃ 1.0 in order to fulfill formaldehyde monitoring requirements of the *attestations d'assainissement* provincial effluent permitting program. Because neither of these methods have been validated for applicability to pulp and paper industry effluents, NCASI undertook studies to evaluate whether the methods produce reliable results suitable for use in making regulatory decisions. The results of the studies, reported herein, show that when methanol is added to samples, as specified in both methods for the introduction of surrogate spikes, a unique interaction between constituents in pulp mill effluents and the pentafluorobenzylhydroxylamine (PFBHA) derivatization chemistry converts some of the methanol to formaldehyde and results in a positive bias. The magnitude of this bias varied from mill to mill and, in some instances, over time. Limited efforts to resolve the problem using antioxidants failed to mitigate the bias. Although the bias can be substantially reduced by specifying the use of acetonitrile as the surrogate spike solution solvent, these studies show that application of either of the subject methods will produce a biased result if the effluent contains any residual methanol. Thus, the PFBHA derivatization chemistry should not be used in pulp mill effluents unless it can be documented that the samples contain no methanol. Comparison of the subject methods to other analytical approaches suggests that there may be yet another source of bias, but a full understanding of this phenomenon would require additional research.

KEYWORDS

analytical procedure, formaldehyde, method evaluation, pulp mill effluent

RELATED NCASI PUBLICATIONS

None

ÉVALUATION DES APPROCHES ANALYTIQUES POUR MESURER LE FORMALDÉHYDE DANS LES EFFLUENTS TRAITÉS DES FABRIQUES DE PÂTE

RAPPORT SPÉCIAL N^o 07-03
AVRIL 2007

RÉSUMÉ

Les fabriques québécoises doivent effectuer l'analyse du formaldéhyde dans les échantillons de leur effluent selon la méthode 6252B du *Standard Method* ou la méthode MA 403-SP.O₃ 1.0 afin de répondre aux exigences de suivi du formaldéhyde contenues dans le programme d'attestation d'assainissement en milieu industriel du gouvernement provincial. Étant donné qu'aucune de ces méthodes n'a fait l'objet d'une validation en ce qui concerne leur application pour les effluents de l'industrie des pâtes et papiers, NCASI a mis sur pied des études pour évaluer si ces méthodes produisent des résultats fiables et utilisables dans les processus décisionnels réglementaires. Ce document présente les résultats de ces études qui démontrent que lorsque le méthanol est ajouté aux échantillons (selon les instructions des deux méthodes pour introduire des échantillons qui ont été enrichis avec des étalons analogues ou *surrogate*), une interaction inattendue entre les constituants des effluents des fabriques de pâtes et les produits de dérivation [dérivation effectuée à l'aide de *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA)] entraîne la conversion d'une partie du méthanol en formaldéhyde. Ceci crée un biais positif dont l'ampleur varie d'une fabrique à l'autre et, dans certains cas, selon le temps. Les chercheurs ont mis en œuvre certaines mesures pour résoudre le problème en utilisant des agents antioxydants mais elles se sont avérées inefficaces pour éliminer le biais. Ce dernier peut être réduit significativement en utilisant l'acétonitrile comme solvant dans la solution des échantillons qui ont été enrichis avec des étalons analogues mais les études démontrent que l'utilisation de l'une ou l'autre de ces méthodes produira un résultat biaisé si l'effluent contient toute trace de méthanol résiduel. Par conséquent, les dérivés de PFBHA (obtenus lors des réactions secondaires) ne devraient pas être utilisés pour les effluents de fabriques de pâtes à moins que l'absence de méthanol dans les échantillons ne soit documentée. La comparaison de ces deux méthodes avec d'autres approches analytiques indique qu'il peut aussi exister une autre source de biais mais il est nécessaire d'améliorer les connaissances de ce phénomène dans le cadre de recherches supplémentaires.

MOTS CLÉS

Procédures analytiques, formaldéhyde, évaluation des méthodes, effluent de fabriques de pâtes

AUTRES PUBLICATIONS DE NCASI DANS CE DOMAINE

Aucune

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EVALUATION OF ANALYTICAL APPROACHES FOR THE MEASUREMENT OF FORMALDEHYDE IN PULP MILL TREATED EFFLUENTS

1.0 INTRODUCTION

Analytical methods for formaldehyde in various matrices associated with the forest products industry have been studied by several researchers over the years. Pulping releases a complex mixture of lignin breakdown products from wood. Sarkanen and Ludwig (1971) reported that formaldehyde can be produced from α -guaiacylglycerol- β -aryl ether and/or 1,2-diguaiacyl-1,3-propanediol structures found in lignin under alkaline or acidic conditions. To the extent that these structures may exist in pulping wastewaters, they represent precursors that could generate formaldehyde if derivatization conditions are not carefully controlled.

Elia and Messmer (1992, 1996) and Priha (1996) studied analytical methods for determining free formaldehyde in resin-containing wood and paper dusts. They determined that a derivatization procedure that relied on low pH conditions (e.g., chromotropic acid and 2,4-dinitrophenylhydrazone technique used in EPA Method 8315A (USEPA 1996)) gave results from two to ten times higher than the milder acetyl acetone procedure (pH 6.2). Both research groups were assessing potential formaldehyde exposure from inhalation of wood or paper dust, so they extracted the dust under physiological conditions (e.g., 37°C). Priha noted that even a small shift in pH from 6.2 to 5.7 resulted in an increase in the hydrolysis of resin, releasing 10% more formaldehyde.

Elia and Messmer (1996) also determined that the 2,4-dinitrophenylhydrazone derivatization procedure could result in formaldehyde formation if starch or glucose was present. Because wood contains cellulose and hemicellulose that can behave similarly, caution is indicated in the use of low pH conditions in any formaldehyde procedure where woody debris may be present.

While these studies are not directly applicable to the measurement of formaldehyde at trace levels in wastewaters, they do illustrate the potential for artifact formaldehyde formation during an analytical procedure. This has served as a precautionary note for the forest products industry.

More recently, NCASI collaborated with Columbia Analytical Services, Inc. (Kelso, WA) to conduct exploratory investigations of analytical procedures for formaldehyde in wastewater. EPA 8315A (2,4-dinitrophenylhydrazine derivatization at pH 3 followed by HPLC-UV) and SM 6252B (pentafluorobenzylhydroxylamine hydrochloride derivatization at pH 6 followed by SIM-GC/MS¹) were the primary procedures. NCASI was concurrently investigating benzylhydroxylamine derivatization (pH 5.5), so the samples were also analyzed using that procedure.

Significantly different levels of formaldehyde were measured and reported using the two primary methods. Due to the exploratory nature of the work, it cannot be used to identify which of the methods reported the more correct concentrations of formaldehyde. However, it does support the need to further investigate the methodology to either understand the reasons for the differences or ascertain which method is the most reliable for measuring formaldehyde in forest products industry wastewaters.

As part of the first *attestations d'assainnement* of the Industrial Waste Reduction Program (Programme de réduction des rejets industriels), Quebec mills were instructed to have monthly

¹ SM 6252B normally utilizes GC-electron capture detection (ECD). However, NCASI did not have access to an ECD at the time this work took place so a SIM GC/MS method was used instead.

composite samples of final effluent analyzed for formaldehyde by either Standard Method (SM) 6252B (APHA, AWWA, and WEF 1998) or MA 403-SP.O₃ 1.0 (CEAEQ 2003).

To the best of NCASI's knowledge, no published study reports validate the applicability of these methods to pulp and paper mill wastewaters. SM 6252B states that it is for the measurement of aldehydes (including formaldehyde) in raw water (e.g., river water) and drinking water, but makes no mention as to its potential applicability to industrial wastewaters. MA 403-SP.O₃ 1.0 specifies that it is applicable for the measurement of ozonation by-products in drinking water. Because of the complexity of pulp mill wastewaters, it is imperative that analytical procedures be thoroughly tested.

Because of the lack of experience with the use of these methods on pulp mill effluents, and because of the importance of basing regulatory decisions on sound science and reliable analytical measurements, it was decided that a more thorough evaluation of the methods prescribed in the Quebec *attestations d'assainissement* pulp mill effluent sampling program was needed. Thus, at the direction of the NCASI Canadian Steering Committee, NCASI undertook an evaluation of SM 6252B and MA 403-SP.O₃ 1.0. This report summarizes the significant findings of that evaluation.

The focus of the work reported herein was to further evaluate whether the subject methods have biases, with particular attention to concerns that the analytical procedures themselves might produce formaldehyde from other substances in pulp mill effluents. The study was not intended to optimize the procedures nor to correct any problems identified. However, where the work provided indications of potential improvements to the subject procedures, they are included in Section 5 of this report. Results reported herein will be helpful in the design of future studies intended to develop and validate appropriate analytical procedures for measuring formaldehyde in pulp mill wastewaters.

2.0 MATERIALS AND METHODS

2.1 Materials

- Bakerbond™ SPE Octadecyl (C₁₈) Disposable Extraction Columns, 6 mL w/ 1000 mg/column, Product No. 7020-07
- Methanol and hexane, Burdick and Jackson, pesticide grade
- Acetonitrile, Burdick and Jackson, HPLC grade
- *O*-(2,3,4,6-pentafluorobenzyl)-hydroxylamine hydrochloride, Aldrich
- Formaldehyde, (methanol free) 10% aqueous solution, Ultrapure EM Grade, for histological uses
- All other reagents, ACS reagent grade
- Deionized water prepared fresh daily using a Barnstead purification system
- ¹³CD₃OD, Cambridge Isotopes

2.2 Standard Method 6252B-SIM

NCASI performed SM 6252B as written except for the following modifications.

- The surrogate standard was prepared in acetonitrile. Recoveries were found to be variable from mill type to mill type while being consistent (sometimes consistently low or high) for a given matrix. Formaldehyde matrix spikes were routinely high, so it was determined that 2,3,5,6-tetrafluorobenzaldehyde is not a good surrogate for formaldehyde in pulp and paper mill effluents. Because it was not the intent of this study to optimize SM 6252B, this was not pursued further.

- Histological grade (i.e., methanol free) 10% aqueous formaldehyde was used to prepare calibration standards as well as matrix spiking standards.
- Extracts were analyzed by GC/MS operated in the selected ion mode. The formaldehyde 2,3,5,6-tetrafluorobenzaldehyde surrogate pentafluorobenzoyloximes were quantified at m/z 181, and the 1,2-dibromopropane internal standard was measured at m/z 121.

2.3 Standard Method 6252B

Columbia Analytical Services, Inc. performed SM 6252B as written except for the following modifications.

- The surrogate standard was prepared in acetonitrile. However, because of a large co-eluting interference, quantification of the surrogate was not reliable.
- Initially, an aqueous formaldehyde stock solution was prepared by heating paraformaldehyde in a round-bottom flask while sweeping it with nitrogen. The nitrogen stream was passed through a chilled midjet impinger filled with water. Prior to use in preparing a matrix spiking solution, the formaldehyde concentration was measured using ASTM D 6303 (ASTM 1998). When it was discovered that histological grade formaldehyde was methanol free, it was used to prepare matrix spiking solutions.
- Because there was no reason to believe that there was chromatographic interference in the ECD analyses (confirmed by split samples run by NCASI using GC/MS SIM detection), dual column confirmation was omitted.

2.4 EPA SW-846 Method 8315A

Columbia Analytical Services, Inc. performed EPA Method 8315A as written except that the sample volume was 20 mL. This resulted in a nominal reporting limit of approximately 10 $\mu\text{g/L}$.

2.5 Method MA 403–SP.O₃ 1.0

Bodycote (Montreal, Quebec) performed MA 403–SP.O₃ 1.0 with adaptations that cannot be disclosed, given that the laboratory considers them proprietary. NCASI required that Bodycote further modify the procedure to use acetonitrile instead of methanol for the surrogate spiking solvent.

2.6 C₁₈-SPE Cleanup

2.6.1 SPE Pre-Wash

The solid phase extraction (SPE) cartridge was pre-eluted with 5 mL of acetonitrile. The cartridge was not allowed to go dry. It was then washed three successive times with 1 mL portions of deionized water, again, not allowing the cartridge to go dry.

2.6.2 Sample Cleanup

A 20 mL portion of sample was passed through the C₁₈-SPE cartridge, taking care not to let the cartridge run dry. The cartridge was then washed with two 2 mL portions of deionized water followed by a 1 mL portion of deionized water. The washes were combined with the cleaned up sample and then analyzed by the appropriate analytical procedure. Note that the surrogate was not added prior to cleanup because it was found to be too lipophilic to be a meaningful surrogate for the highly water soluble formaldehyde.

2.7 Chemical Ionization MS

The chemical ionization MS spectra of the acetaldehyde PFOA and the $^{13}\text{CD}_3\text{OD}$ spike sample PFBHA derivatized extract were collected on a 6890/5973N Mass Spectrometer with chemical ionization source running in the positive CI mode and methane as the reagent gas. The mass scan range was 90 to 250 m/z. The separations were achieved using a 30m x 0.25 μm Phenomenex ZB-5 column.

3.0 EVALUATIONS OF THE EFFECT OF ADDING METHANOL TO A SAMPLE PRIOR TO ANALYSIS

Early in development of the C_{18} -SPE cleanup procedure (discussed further in Section 4) it was observed that analyses of bleached (Mill A) and unbleached (Mill B) kraft mill effluent matrix spikes using SM 6252B-SIM resulted in extremely high recoveries. After further investigation, it was determined that this was associated with the methanol solvent used to prepare the formaldehyde spiking solution. The apparent high formaldehyde concentrations could be replicated by simply spiking the sample with methanol.

One hypothesis for this observation was that the methanol was being oxidized to formaldehyde by some unknown oxidant in the sample matrix. This would explain why the phenomenon was not observed in calibration solutions prepared by spiking known amounts of formaldehyde into reagent water followed by derivatization, extraction, and analysis procedures identical to those applied to samples.

A simple test of this hypothesis involved spiking a sample of Mill A effluent with ethanol. The spiked sample was then derivatized, worked up, and analyzed in the normal manner. As illustrated in Figure 3.1, this resulted in the characteristic double peak (the E and Z acetaldehyde pentafluorobenzoyloxime (PFBO) isomers) of an acetaldehyde-PFBO derivative where none was observed previously (i.e., in the unspiked sample). This demonstrated that another simple primary alcohol (ethanol) can be converted to its corresponding aldehyde (acetaldehyde) during the course of analysis of pulp and paper mill effluent samples using SM 6252B.

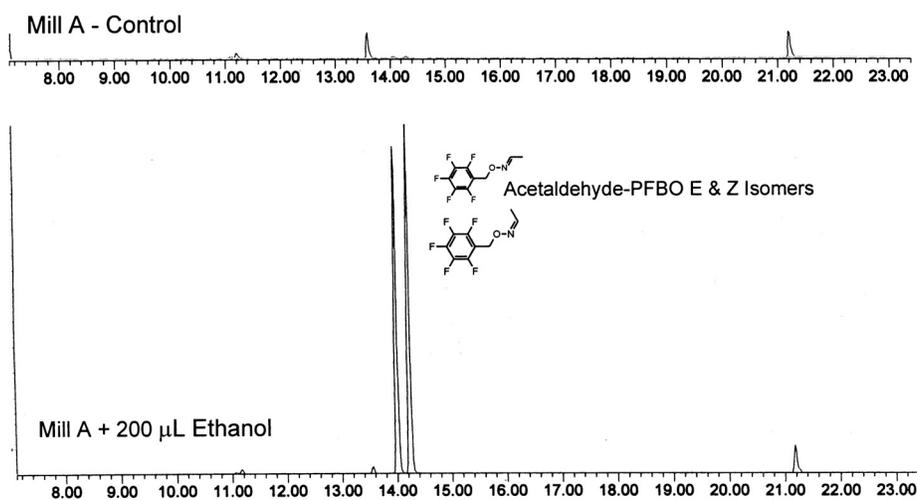


Figure 3.1 Chromatograms of Mill A Effluent Analyzed by SM 6252B-SIM without and with Addition of Ethanol

To further confirm this hypothesis, a fresh aliquot of Mill A effluent taken on another day was spiked with $^{13}\text{CD}_3\text{OD}$ and was derivatized and extracted by the procedures described in SM 6252B. Prior experience running PFBHA-derivatized aldehydes using electron impact MS suggested that it was unlikely that strong molecular ions would be observed and the predominant pentafluorotropylium ion that is the base peak would not retain the ^{13}C carbon nor deuterium atoms. Therefore, the extract was analyzed by chemical ionization MS. Figure 3.2 shows the mass spectrum of an unlabeled formaldehyde PFBO derivative and the mass spectrum of the peak observed at the retention of the formaldehyde-PFBHA derivative from the $^{13}\text{CD}_3\text{OD}$ spiked sample. The molecular ion at three mass units higher than the unlabeled formaldehyde molecular ion proves conclusively that the $^{13}\text{CD}_3\text{OD}$ was converted to $^{13}\text{CD}_2\text{O}$ (labeled formaldehyde).

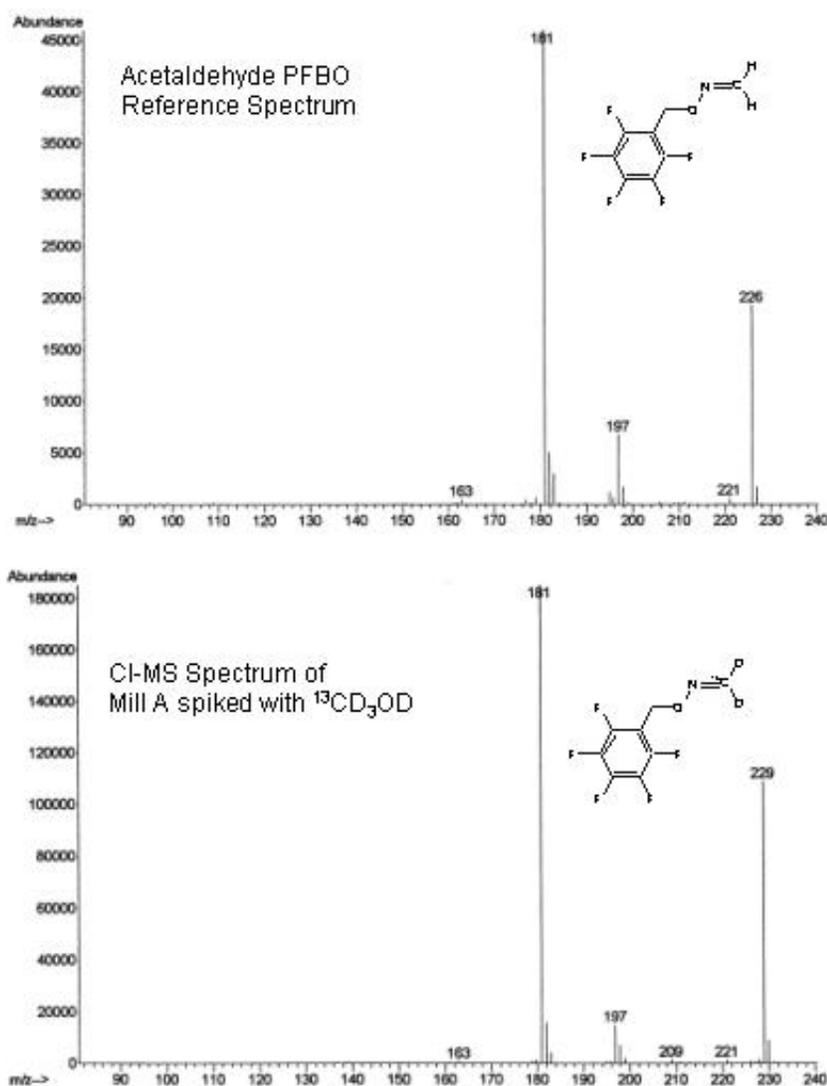


Figure 3.2 Chemical Ionization Mass Spectrum of Unlabeled Formaldehyde Pentafluorobenzoyloxime (PFBO) Derivative and PFBO Derivative Resulting after Spiking Sample with $^{13}\text{CD}_3\text{OD}$

In another experiment, fresh samples from Mills A and B were analyzed by Columbia Analytical Services, Inc. using EPA 8315A both with and without addition of methanol equivalent to the volume normally added in SM 6252B. Concurrently, splits of the samples were analyzed by NCASI using SM 6252B-SIM for comparison. The results are summarized in Table 3.1. Although the results for Mill A analyzed using EPA 8315A might suggest a slight increase in measured formaldehyde when methanol was added, it is more likely that the increase from non-detect at 11 ppb to detect at 13 ppb is simply measurement variability. It is quite evident that the increase from 12.6 to 2600 ppb using SM 6252B-SIM was not observed by Columbia Analytical Services, Inc. using EPA 8315A. Similarly, there was no indication of increased measured formaldehyde when Mill B samples were spiked with methanol and EPA 8315A was used for the analysis. These results indicate that the apparent increase in measured formaldehyde associated with the addition of methanol to a pulp mill effluent is uniquely associated with PFBHA derivatization chemistry. This observation is extremely important because it clearly indicates that if there is any methanol in a pulp mill effluent, application of the PFBHA chemistry will result in a biased measurement of formaldehyde. Verification of an unbiased formaldehyde measurement in pulp mill effluent would require demonstration of the absence of methanol at comparable detection limits.

Table 3.1 Results of Analysis of Effluents by Methods EPA 8315A and SM 6252B-SIM with and without Addition of Methanol

| Treatment | Concentration ($\mu\text{g/L}$) | |
|--|-----------------------------------|--------------|
| | EPA 8315A | SM 6252B-SIM |
| Mill A | ND(<11) | 12.6 |
| Mill A + methanol | 13 | 2600 |
| Mill A + 100 ppb matrix spike (% recovery) | 94% | 84% |
| Mill B | ND(<11) | 18.6 |
| Mill B + methanol | ND(<11) | 318 |
| Mill B+ 100 ppb matrix spike (% recovery) | 92% | 88% |

As part of a standard addition experiment undertaken to better understand the nature of the conversion of methanol to formaldehyde, a Mill A effluent was spiked with several different volumes of methanol and then analyzed by SM 6252B-SIM. The results are summarized in Figure 3.3. A very large increase in measured formaldehyde was observed for the first 50 μL of methanol spiked. Although additional increases were observed for the 200 and 800 μL spikes, they were not directly proportional. SM 6252B and MA 403-SP.O₃ 1.0 both specify that the surrogate standard be made up in methanol. SM 6252B specifies a 10 μL spike into a 20 mL sample, while MA 403-SP.O₃ 1.0 specifies a 40 μL spike into a 34 mL sample. Thus, the rote application of either method will lead to high biased formaldehyde results when the methods are applied to pulp and paper mill effluents.

The bias associated with spiking surrogates prepared in methanol may be readily eliminated by preparing those standards in acetonitrile. In fact, EPA's Method 556.1 for drinking water (USEPA 1999), which is based on the same basic *in situ* PFBHA derivatization chemistry, specifies that standards be prepared in acetonitrile.

However, there is another aspect of the methanol bias that must be taken into consideration. The 37% formalin solutions from which calibration and matrix spiking solutions are prepared is most often stabilized with between 7 and 15% methanol. Thus, any matrix spiking solution would contain both formaldehyde and methanol. In order to further examine the significance of this, another spiking study was performed using very small quantities of methanol. A fresh portion of Mill A effluent was spiked with smaller quantities of methanol and then analyzed by SM 6252B-SIM. The data, shown in

Figure 3.4, indicate a very large increase in measured formaldehyde (from 15.2 to 822 $\mu\text{g/L}$) associated with a 0.5 μL methanol spike. Thus, the quantity of methanol present in commercially prepared formaldehyde spiking solutions would be more than enough to significantly bias a matrix spiked pulp mill effluent measurement made using SM 6252B or MA 403-SP.O₃ 1.0.

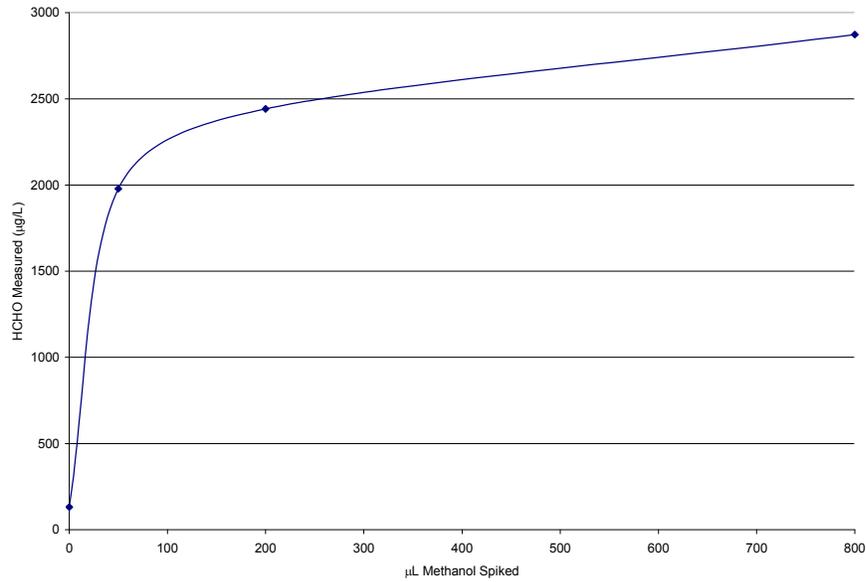


Figure 3.3 Increase in Measured Formaldehyde vs. Volume of Methanol Spike When Analyzed by SM 6252B-SIM

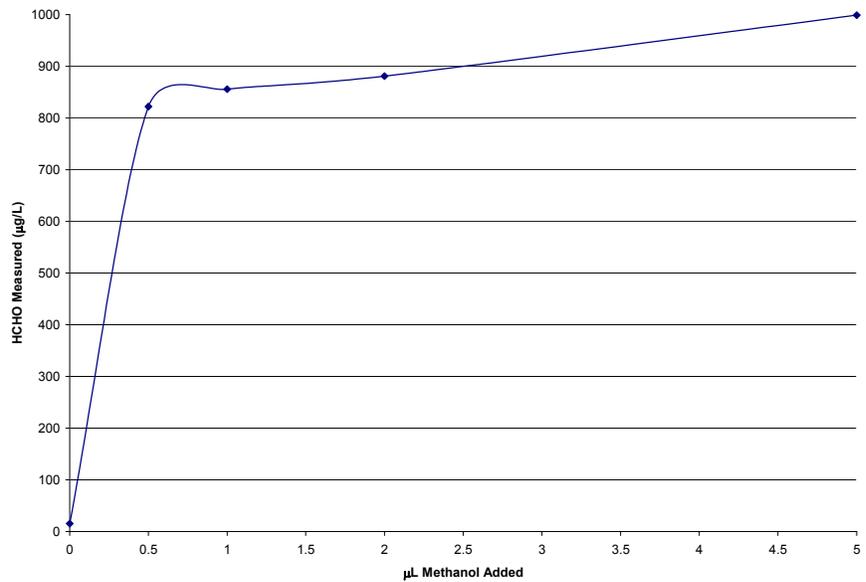


Figure 3.4 Increase in Measured Formaldehyde with Small Additions of Methanol When Analyzed by SM 6252B-SIM

Here again, a solution is readily available. Histological grade formaldehyde solutions are, by necessity, methanol-free. Analysts can purchase these solutions for preparation of matrix spiking solutions. However, methanol is normally added to stabilize the formaldehyde, so additional quality control calibration checks should be implemented by the analyst until the stability of formaldehyde standards prepared in this manner can be ascertained.

In an effort to find an alternative solution to the methanol artifact bias and to gain further understanding as to its nature, a series of experiments was performed to determine whether common antioxidants would mitigate the problem. It also seemed logical to determine whether a commonly used preservative (copper sulphate) would eliminate or otherwise affect the bias. If copper sulphate did not impact measurement procedures, it would be worth pursuing as a means of extending the holding time from the 48 hours specified in SM 6252B. Accordingly, Mill A effluent was analyzed with neither preservative nor methanol addition using SM 6252B-SIM concurrently with splits of the same sample treated with sodium thiosulphate, ascorbic acid, sodium bisulphite, and copper sulphate both with and without the addition of methanol. These results are summarized in Table 3.2.

Table 3.2 Evaluation of the Effects of Common Antioxidants and a Preservative on Measured Formaldehyde Levels by SM 6252B-SIM with and without Addition of Methanol

| Treatment | Formaldehyde Concentration ($\mu\text{g/L}$) | |
|---------------------|--|--------------------------------|
| | without methanol | with 50 μL methanol |
| None (control) | 11.3 | 1160 |
| Sodium thiosulphate | 13.2 | 1090 |
| Ascorbic acid | 38.9 | 523 |
| Sodium bisulphite | 4 | 75.6 |
| Copper sulphate | 40 | 120 |

Sodium thiosulphate seemed to have no effect on the unspiked samples or on the methanol-spiked samples. Although ascorbic acid reduced the methanol artifact bias by a factor of two, it did not completely eliminate it and caused an over threefold increase for the unspiked sample. Sodium bisulphite had the greatest effect in reducing the methanol bias, but it was still unable to completely eliminate it. It also seemed to have an adverse effect on the unspiked sample result, although this probably deserves further investigation. Therefore, none of the antioxidants was completely effective in mitigating the methanol artifact and no further work along these lines was pursued.

Although the reason is not apparent, copper sulphate significantly reduced but did not completely eliminate the methanol bias. Furthermore, it caused an almost fourfold increase in the unspiked sample result. In a follow-up experiment, calibration curves prepared with and without copper sulphate were essentially identical, indicating that copper sulphate had no effect on the calibration curve. This discouraging result indicated further complications with SM 6252B, the investigation of which is beyond the scope of the current work.

Apparently, no preservatives were used in the early *attestations d'assainissement* sampling, but holding times may have been as long as 10 days. In the latter part of the sampling, a mercuric chloride (HgCl_2) preservation strategy was implemented. Because of the surprising result observed for the other sample preservative tested (copper sulphate), it was deemed prudent to evaluate the potential impact of that strategy. Furthermore, it seemed important to understand the methanol artifact bias over time, both with and without the addition of mercuric chloride. A fresh sample of Mill A effluent was collected and carefully split. Half the aliquots were preserved in a manner analogous to that used in the latter stages of the *attestations d'assainissement* program and the other half were unpreserved. All were refrigerated. The samples were analyzed by SM 6252B-SIM on the day of collection (day 0)

and at intervals of 1, 2, 5, and 6 days. Sample aliquots were analyzed both with and without methanol spikes at each time interval. Although these measurements were made using SM 6252B-SIM, the quantities of HgCl₂ and methanol were selected to mimic the measurements made using MA 403–SP.O₃ 1.0 during the previous sampling in Quebec. Results are summarized in Table 3.3.

Table 3.3 Effects of Holding Time and Mercuric Chloride and Methanol Addition on Measured Formaldehyde by SM 6252B-SIM

| Treatment | Formaldehyde Concentration (µg/L) | | | | |
|-----------------------------------|-----------------------------------|-------|-------|-------|-------|
| | Day 0 | Day 1 | Day 2 | Day 5 | Day 6 |
| None (control) ^a | 23.2 | 18.9 | 16.9 | 15.7 | 15.6 |
| w/ HgCl ₂ ^a | 154 | 68.1 | 49.3 | 52.3 | 50.8 |
| w/ methanol | 1170 ^a | 1090 | 982 | 1170 | 203 |
| w/ HgCl ₂ and methanol | NA | 1840 | 1650 | 1670 | 1650 |

^a mean of duplicate analyses

Although there appears to be a slight drop in concentration within the first 24 hours for the unspiked unpreserved control sample, it is not compelling evidence of degradation. This is especially true in that it is not clear that formaldehyde is not actually being formed during the measurement process. In this experiment, use of HgCl₂ caused an almost sevenfold increase in the measured concentration of formaldehyde relative to the control. The magnitude of the methanol artifact bias was relatively constant out to five days, after which there was a significant drop. Furthermore, the HgCl₂ was observed to almost double the magnitude of the bias associated with the presence of methanol. Although these observations cannot be rationalized at this time, it is clear that the use of HgCl₂ as a preservative requires significant additional investigation and validation.

The next aspect of the methanol artifact bias to be investigated was its magnitude for different types of pulp mill effluent. Samples from several different mill types were collected and analyzed within 48 hours (refrigerated but otherwise unpreserved) without addition of methanol, with addition of methanol, with addition of HgCl₂, and with addition of both HgCl₂ and methanol. Methanol spike volumes were consistent with the volumes of surrogate spike solution specified by the respective methods. Results for four U.S. Pacific Northwest mills analyzed by SM 6252B-SIM are summarized in Table 3.4 and results for five Quebec mills analyzed by MA 403–SP.O₃ 1.0 are summarized in Table 3.5. NCASI ran concurrent matrix spikes on each sample tested and these data are also summarized in Table 3.4.

With the sole exception of Mill C, all samples showed an increase in measured formaldehyde levels relative to a control when HgCl₂ preservative solution was added. The increases ranged from factors of 1.4 to 2.7. Mill F was sampled two different times and showed 2.4- and 2.7-fold increases. Although the range of factors within a given mill type is narrower, it is not possible to predict with certainty what the factor will be for a specific mill. Given the overall range of increases observed, there is no indication that this phenomenon is better or worse for the two different methods.

The addition of methanol in quantities simulating the volumes normally used for surrogate spikes resulted in increases of measured formaldehyde relative to the control by factors of 1.6 to 206. In the two analyses of Mill F, the factors were highly variable: an 18-fold increase for one analysis and a 3.4-fold increase for the other. Here again, the amount of increase cannot be reliably predicted by mill type. Again, there is no indication that one analytical procedure is any more or less impacted by this phenomenon.

With the exception of Mill C, the combination of both HgCl₂ preservative and methanol simulating the surrogate spike resulted in the largest increases in measured formaldehyde, ranging from 5.4-fold to 224-fold. The lack of a consistent pattern makes it impossible to reliably predict the magnitude of the increase on a given sample or on samples from the same mill collected at different times.

Table 3.4 Results of Analyses of Different Mill Types Using SM 6252B-SIM

| Procedure/Treatment | Formaldehyde Concentration (µg/L) | | | |
|-----------------------------------|---|--|--------------------------------------|--|
| | Mill A Integrated BK ^a | Mill B Integrated UBK ^b | Mill C Integrated Deink/Tissue | Mill D Integrated TMP ^c |
| Mill Type | | | | |
| None (control) ^d | 12.6 | 18.6 | 46.4 | 11.8 |
| w/ HgCl ₂ | 29.4 | 29.2 | 46.2 | 23.3 |
| w/ methanol | 2600 | 318 | 72 | 307 |
| w/ HgCl ₂ and methanol | 2820 | 600 | 61.6 | 329 |
| 100 ppb matrix spike recovery | 84% | 88% | 100% | 90% |

^a bleached kraft

^b unbleached kraft

^c thermomechanical pulp

^d mean of duplicate analyses

Table 3.5 Results of Analyses of Different Mill Types Using MA 403-SP.O₃ 1.0

| Procedure/Treatment | Formaldehyde Concentration (mg/L) | | | | | |
|-----------------------------------|-----------------------------------|---------------------------|---------------------------|---|--|---|
| | Mill E BK ^a | Mill F BK ^a | Mill F BK ^a | Mill G Integrated TMP ^b w/ Deinking | Mill H Integrated TMP ^b | Mill I Integrated Groundwood and Chemical TMP ^b |
| Mill Type | | | | | | |
| None (control) | 0.04 | 0.13 | 0.15 | 0.03 | 0.03 | 0.39 |
| w/ HgCl ₂ | 0.06 | 0.31 | 0.41 | 0.08 | 0.06 | 0.56 |
| w/ methanol | 0.9 | 2.3 | 0.51 | 0.26 | 0.60 | 0.73 |
| w/ HgCl ₂ and methanol | 1.2 | 5.2 | 0.81 | 0.27 | 0.60 | 3.0 |

^a bleached kraft

^b thermomechanical pulp

4.0 COMPARISON OF RESULT OF SAMPLES ANALYZED USING DIFFERENT PROCEDURES

Discovery of the methanol artifact and its associated issues with respect to preservatives, although fortunate, was not the focus of the original study design. The initial concern was potential formation of formaldehyde from other substances present in pulp mill effluents during the derivatization step of SM 6252B, as evidenced by the early NCASI exploratory work. This presents a unique method validation challenge. Matrix spike recovery is a commonly used tool for validating recovery, but would not reveal the formation of formaldehyde during derivatization chemistry (formation would be present in the unspiked sample used to establish the background level as well as in the matrix spike sample). If one knew the formaldehyde precursor, simple spikes of that substance would suffice to demonstrate the artifact, as was observed for the methanol artifact. Thus, the situation called for a different validation strategy.

The strategy selected was to have aliquots of a sample analyzed by multiple analytical procedures. Every practical effort was made to focus the experiments on the analytical artifact problem. Ideally, the procedures used would employ completely different chemistries, separation techniques, and detection procedures. Finally, all measurements would be supported by appropriate QA/QC.

The interpretation was that if several uniquely different analytical procedures converged on the same result (within experimental error) it would be evidence of the true concentration of formaldehyde in the sample. The focus of the work was to identify potentially significant artifacts, so it was not deemed necessary (or within the study budget) to develop a statistical demonstration of comparability. Therefore, single analyses were employed.

While implementation of this validation strategy on a number of different mill types was originally envisioned, NCASI found it difficult to find mills with measurable levels of formaldehyde. However, it was possible to implement the approach on one bleached and one unbleached mill effluent that had levels of formaldehyde high enough to make comparisons. It should be noted that all of this work was performed using procedures that did not introduce methanol into the sample so the methanol artifact could be separated from any other artifacts.

SM 6252B, SM 6252B-SIM, EPA Method 8315A, ASTM Method D 6303, and EDANA Method 212.0-96 (EDANA 2002) were selected. Table 4.1 summarizes some of the features of those methods.

SM 6252B was one of the procedures specified by the Quebec Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP). SM 6252B-SIM was included to add a control for possible co-eluting electron capture interferences, although that was not believed to be the problem. This methodology employs *in situ* derivatization with pH 6 buffering, *O*-(2,3,4,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) at 45°C for 105 minutes to form pentafluorobenzylloxime derivatives, quenching with concentrated H₂SO₄, extraction with hexane, back washing with dilute H₂SO₄, and analysis by GC/ECD. The NCASI adaptation of the procedure simply substitutes GC/MS-SIM as the final detection device.

EPA Method 8315A (implemented by Columbia Analytical Services, Inc.) employs *in situ* derivatization using pH 2 buffering and 2,4-dinitrophenylhydrazine at 40°C for 60 minutes. The 2,4-dinitrophenylhydrazone derivatives are isolated from the water using C₁₈-SPE with acetonitrile elution. Final separation is performed by reverse phase HPLC with UV detection.

ASTM D 6303 utilizes pH 9.5 and acetylacetone at 60° for 10 minutes to form lutidine from formaldehyde via the Hantzsch reaction. For coloured samples such as pulp mill effluents, the lutidine is extracted in *n*-butanol and measured by UV-VIS-spectrophotometry at 412 nm. Unfortunately, due to the low apparent formaldehyde levels in the samples and the method's higher detection limit, no useful data were obtained.

EDANA 212.0-96 was probably the most unique procedure. It employs direct injection of a filtered sample on a C₁₈-reverse phase HPLC column to separate formaldehyde from any interferences and almost all other organics (formaldehyde is essentially not retained by the column, whereas potential interferences and formaldehyde precursors are somewhat or completely retained). The method then uses post-column derivatization via the Hantzsch reaction to form lutidine (see above description of ASTM D 6303) that is subsequently measure by UV-VIS detector at 412 nm. Unfortunately, implementation of this procedure at this phase of the study was not logistically practical.

Table 4.1 Summary of Formaldehyde Analytical Methods under Consideration

| SM 6252B | SM 6252B-SIM | MA 403-SP.O ₃ 1.0 | EPA 8315A | ASTM D 6303-98 | EDANA 212.0-96 |
|--|--|--|--|---|---|
| PFBHA reaction to form oxime derivative | PFBHA reaction to form oxime derivative | PFBHA reaction to form oxime derivative | 2,4-DNPH reaction to form hydrazone derivative | 2,4-pentanedione (Nash reagent) reaction to form lutidine | Post-column reaction with 2,4-pentanedione (Nash reagent) |
| pH 6, 45°C, 105 min | pH 6, 45°C, 105 min | pH 5, 45°C, 120 min | pH 5 (for HCHO), 40°C, 60 min | 60°C, 10 min, pH 9.5 | 95°C |
| Conc. H ₂ SO ₄ quench, hexane extraction with H ₂ SO ₄ cleanup | Conc. H ₂ SO ₄ quench, hexane extraction with H ₂ SO ₄ cleanup | Conc. H ₂ SO ₄ quench, hexane extraction with H ₂ SO ₄ cleanup | 2 g C ¹⁸ -SPE, CH ₃ CN elution or 3x20 mL DCM extraction | n-butanol extraction | C18 HPLC column cleanup before derivatization |
| DB-5 GC/ECD DB-1701 GC/ECD confirmation column | DB-5 GC/MS-SIM | DB-5 GC/ECD | C ¹⁸ HPLC-UV at 360 nm | UV spectrophotometry at 412 nm | HPLC-UV-VIS at 412 nm |

It was noted that it may be possible to approximate a key feature of EDANA 212.0-96 (i.e., separation of formaldehyde from other sample constituents prior to applying a given derivatization chemistry) by passing a sample through a C₁₈-SPE cartridge. Because formaldehyde is essentially not retained, small reagent water washes are all that is needed to flush the last interstitial traces of the sample off the cartridge. The combined sample and washes could then be analyzed by either SM 6252B (or the NCASI adaptation) or EPA 8315A. Ideally, this would remove any formaldehyde precursors prior to applying derivatization chemistry; however, without knowing the specific substances, quantitative removal cannot be proven and one can only infer their removal by a reduction in post-column measured formaldehyde. Obviously, matrix spikes run through the same procedure would be needed to verify quantitative recovery of authentic formaldehyde in the sample.

At this phase of the project, Columbia Analytical Services, Inc. performed SM 6252B, C₁₈-SPC cleanup followed by SM 6252B, EPA 8315A, C₁₈-SPE cleanup followed by EPA 8315A, and ASTM D 6303 (not reported here because detection limits were too high for the samples). Samples of Mill A and Mill B effluent were collected on one day and all analyses were performed the following day. The results of this series of experiments are summarized in Table 4.2.

Table 4.2 Comparison of Measured Formaldehyde Using Different Analytical Procedures and a Cleanup Procedure

| Procedure/Treatment | Formaldehyde Concentration ($\mu\text{g/L}$) | |
|--|--|--------|
| | Mill A | Mill B |
| SM 6252B | 110 | 122 |
| EPA 8315A | 38 | <20 |
| C ₁₈ -SPE cleanup/SM 6252B | 18 | <20 |
| C ₁₈ -SPE cleanup/EPA 8315A | 17 | <20 |
| SM 6252B + 20 μL methanol | 220 | 290 |

Examining the results of normal analyses of the samples (i.e., without cleanup), it appears that SM 6252B gives results from approximately three to greater than six times higher than those of EPA 8315A. Unfortunately, due to a miscommunication of the standardized concentration of the methanol-free formaldehyde solution used for the matrix spike, the spike levels used for SM 6252B analyses were either approximately equal to or lower than background levels in the samples, confounding interpretation of the experiment. Laboratory control sample recovery for SM 6252B analyses was 98%, but recoveries for unbleached and bleached mill effluent analyses were 27% and 53%, respectively. Because background levels measured by EPA 8315A are so much lower, the accidental low spike levels were less troublesome. For this method, laboratory control sample recovery was 94% and unbleached and bleached mill effluent recoveries were 120% and 120%, respectively. Note that even if the low spike recoveries are taken as evidence for low bias, the data still support the observation that SM 6252B, despite potential indications of low bias, gives higher results than EPA 8315B.

Turning attention to the C₁₈-SPE cleanup analyses, it is apparent that post-cleanup analyses by SM 6252B gave results that were more consistent with EPA 8315A analyses of the samples without cleanup. Post-cleanup analyses using EPA 8315A were also comparable. In this case, SM 6252B matrix spike recoveries for unbleached and bleached mill effluent analyses were 41% and 74%, respectively, and EPA 8315A recoveries for unbleached and bleached effluent analyses were 56% and 71%, respectively. Here again, the erroneous spike level confounds interpretation. Unbleached sample recoveries are lower than considered desirable, while bleached sample analyses are low but acceptable.

Taken collectively, these data suggest that SM 6252B has a high bias relative to EPA 8315A but this bias can be mitigated through the use of a C₁₈-SPE cleanup. Additional verification with a properly executed QA/QC plan would be desirable. However, although several additional samples were collected from both mills and pre-screened for suitability for a repeat of the experimental design, they never showed levels of formaldehyde above 20 ppb and a repeat experiment was not possible.

On a final note, methanol spikes performed as part of this experiment confirmed the methanol artifact problem in these two samples. This is useful in that it confirms the artifact problem by a second laboratory.

5.0 CONCLUSIONS AND RECOMMENDATIONS

It is clear that addition of methanol (e.g., as a solvent for the surrogate spiking solution or as a stabilizing agent in the primary materials used to prepare matrix spiking solutions) leads to production and subsequent biased measurements of formaldehyde. The data clearly indicate that added methanol is oxidized, forming formaldehyde. Neither the causative agents in the samples nor

the exact mechanisms for this chemistry are known. The magnitude of the bias varied by mill site and from time to time at a given site.

Modest efforts to mitigate the conversion of methanol to formaldehyde using common antioxidants were unsuccessful. In some instances, an antioxidant partially mitigated the methanol oxidation but caused another source of positive bias. Finally, it was demonstrated that use of mercuric chloride further exacerbated the problem, causing even greater bias.

As noted, antioxidants appeared to create new, unexpected sources of bias that are not readily understood. In an effort to test potential new sample preservations and in testing the sample preservation used in the *attestations d'assainnement*, it was determined that all conditions tested cause new, poorly understood sources of bias.

Scrupulous avoidance of methanol in the analytical procedure through the use of acetonitrile as the solvent for the surrogate spiking solution and histological grade formaldehyde for the preparation of matrix spike solutions should effectively and simply avoid the methanol oxidation bias. However, it appears that preservatives such as mercuric chloride and copper sulphate and antioxidants such as sodium thiosulphate, ascorbic acid, and sodium bisulphite should be avoided, as they lead to biased measurements.

There is further evidence of a positive bias associated with pentafluorobenzylhydroxylamine derivatization-based analytical procedures. This is seen in the comparison of results using this methodology vs. a method using a different derivatization technique (e.g., EPA 8315A) and in the reduction in measured formaldehyde when a C₁₈-SPE cleanup procedure is employed. It is recommended that this be investigated further, but until these issues are fully resolved, consideration should be given to incorporating the C₁₈-SPE cleanup in all measurements utilizing PFBHA chemistry. Furthermore, because the current surrogate cannot be used to assure that the analyte is not being recovered, all measurements should be performed with concurrent matrix spikes prepared from histological grade formaldehyde.

Considering the distinct possibility that there may be trace levels of methanol present in treated effluents, utilization of PFBHA derivatization chemistry will result in biased measurements. This may, in fact, be the apparent bias observed when results of PFBHA-based procedures are compared to other analytical techniques. It is clear that until the absence of methanol in a pulp mill effluent is demonstrated, one cannot rely upon PFBHA derivatization chemistry to produce an unbiased measurement.

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