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BLANK CORRECTIONS FOR ULTRATRACE ATOMIC ABSORPTION ANALYSIS,(U)
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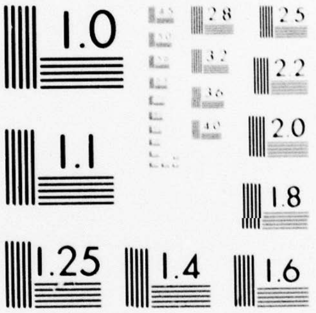

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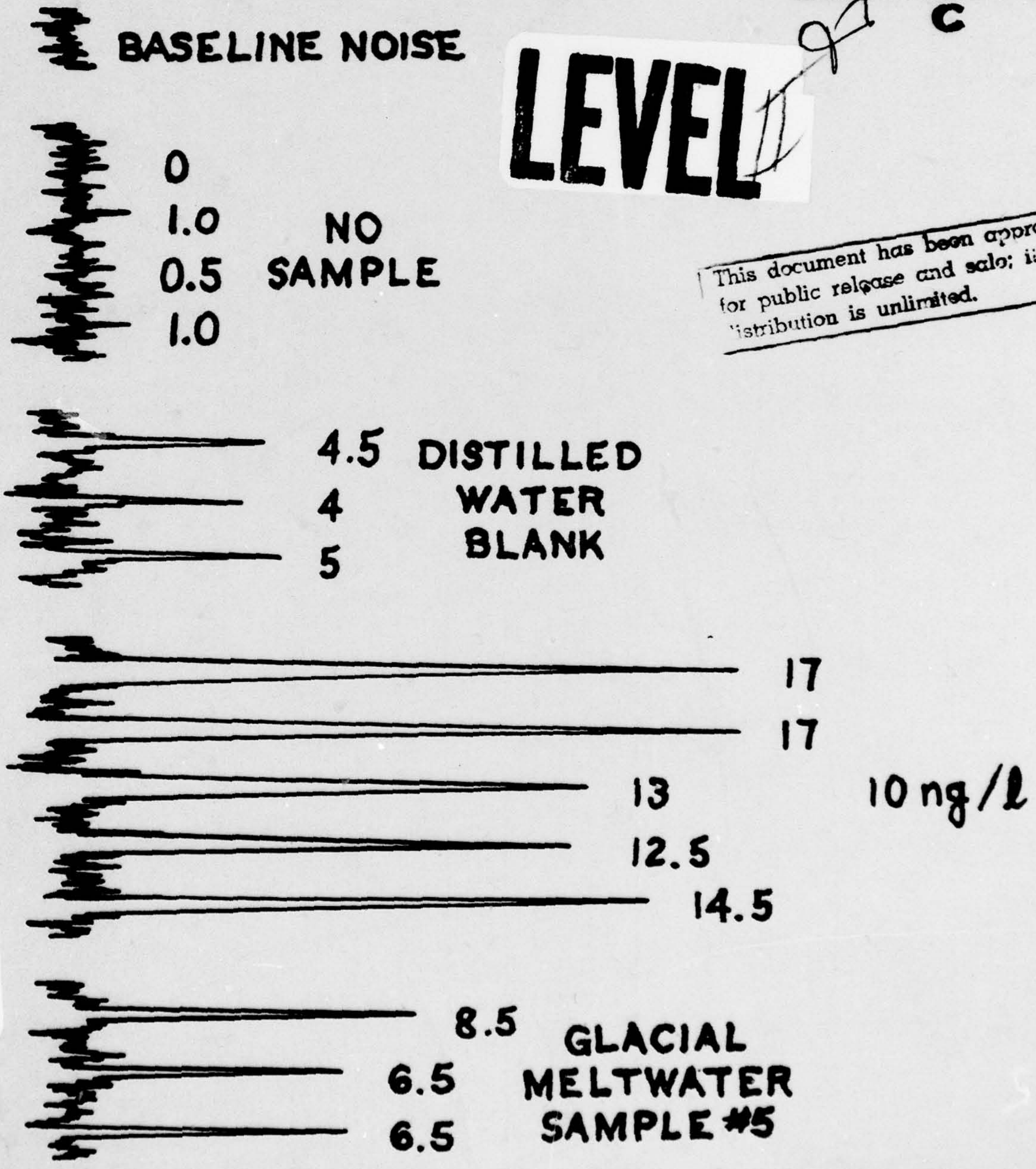
Blank corrections for ultratrace atomic absorption analysis



For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, *published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.*

Cover: Recorder output tracings from flameless atomic absorption analysis of cadmium in blank, standard and polar snow meltwater samples.

CRREL Report 79-3

Blank corrections for ultratrace atomic absorption analysis

James H. Cragin and Steven T. Quarry

January 1979

Prepared for
NATIONAL SCIENCE FOUNDATION
By
UNITED STATES ARMY
CORPS OF ENGINEERS
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE, U.S.A.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

14 **REPORT DOCUMENTATION PAGE**	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER CRREL ~~Report~~ - 79-3 ✓	2. GOVT ACCESSION NO.
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 BLANK CORRECTIONS FOR ULTRATRACE ATOMIC ABSORPTION ANALYSIS	5. TYPE OF REPORT & PERIOD COVERED
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 James H. Cragin ~~and~~ Steven T. Quarry	8. CONTRACT OR GRANT NUMBER(s) 15 NSF-Interagency Agreement DPP78-17165
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS National Science Foundation Washington, D.C. 20550	12. REPORT DATE 11 January 1979
	13. NUMBER OF PAGES 7
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) 12 9p.	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	
18. SUPPLEMENTARY NOTES	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Acid blanks Adsorption Atomic absorption Blanks	Heavy metals Spectrophotometry Standards Trace elements

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Both flame and flameless atomic absorption (AA) measurements require a distilled water blank correction. This correction is due to the analyte contained in the distilled water used to prepare the standards and not, as commonly thought, to the reference "blank" used to zero the instrument. Flameless AA analyses of acidified heavy metal samples generally require additional corrections for the furnace deflection blank and for an acid blank. To prevent adsorption losses, the acid blank should be determined by extrapolation of a series of acid dilutions in distilled water.

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PREFACE

This report was prepared by James H. Cragin, Chemist, Snow and Ice Branch, and Steven T. Quarry, Physical Sciences Technician, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by the National Science Foundation under Interagency Agreement DPP78-17165.

G.A. Klouda of the National Bureau of Standards and D. Leggett of CRREL technically reviewed the manuscript.

BLANK CORRECTIONS FOR ULTRATRACE ATOMIC ABSORPTION ANALYSIS

James H. Cragin and Steven T. Quarry

INTRODUCTION

Most methods of quantitative chemical analysis are relative in that they involve the measurement of the difference between sample and "blank" (distilled water) readings, and a subsequent comparison of this difference with readings from standards. Accurate chemical results depend not only upon the analytical method and standards used but also upon the magnitude and variability of the analyte concentration in the blank. In addition to being constant and reproducible, the blank should have a sufficiently low concentration of analyte so that the sample may be distinguished from it. For many analyses the blank analyte concentration is usually low enough (<1% of the sample concentration) so that it can be neglected. However, for trace (µg/l) and ultratrace (ng/l) determinations, blank concentrations can be significant even with the most refined water and reagent purification systems.

In this report, blank corrections will be discussed with regard to atomic absorption (AA) spectrophotometry since it is one of the most frequently used techniques of trace analysis. Many of the arguments given, however, apply equally well to other methods of analysis.

EXPERIMENTAL

Cadmium was selected for analysis because of the high sensitivity of flameless atomic absorption for this element. All laboratory work was performed within Class 100 laminar-flow clean air stations. Blanks of doubly-distilled deionized water (DDW) and acid blanks, consisting of Ultrex HNO_3 (J.T. Baker Chemical Co.) in DDW, were prepared and stored in Nalgene 2-oz (60-ml) Teflon FEP bottles. These bottles, and all other plastic labware that came in contact with blanks or standard solutions, were cleaned by 1) rinsing with distilled water (DW), 2) ultrasonically cleaning in electronic grade acetone, 3) leaching in warm (55°C) concentrated redistilled HNO_3 (G. Frederick Smith Chemical Co.) for 48 hours, 4) rinsing twice with DW, 5) leaching in 1% (vol) concentrated Ultrex HNO_3 in DDW for 5 days, and finally 6) rinsing thoroughly with DDW.

Cadmium analyses were performed using a Perkin-Elmer Model 403 atomic absorption spectrophotometer and an HGA-2000 Heated Graphite Atomizer located within a Class 100 work station. Sample aliquots of 100 µl were dried at 140°C for 60 s, charred at 370°C for 15 s, and atomized at 1470°C for 15 s. No loss of cadmium occurred during the drying or charring operations. Standards were prepared from a stock solution of cadmium metal in dilute nitric acid.

DISCUSSION

Flame AA

The most common error requiring correction in trace flame AA analysis is due to analyte impurity in the distilled or deionized water (DW) used to prepare the standards. All standards will be high by the amount of analyte in the DW, since DW was used to prepare them. Subsequent calculation of sample concentrations from the high standards will result in erroneously low values for the samples. In addition to the standards' DW blank, another DW blank is needed to physically zero the AA spectrophotometer during operation. Because of the relatively large volumes required, it is often not convenient to use the standards' blank for this purpose. This reference DW blank is also analyzed before and after each standard or sample to compensate for instrument drift at high scale expansions. Standards and samples are then compared to the reference DW blank to obtain a fixed calibration curve. Thus, two different DW blanks exist: a standards' DW blank and a reference DW blank. The effects of blank impurities upon

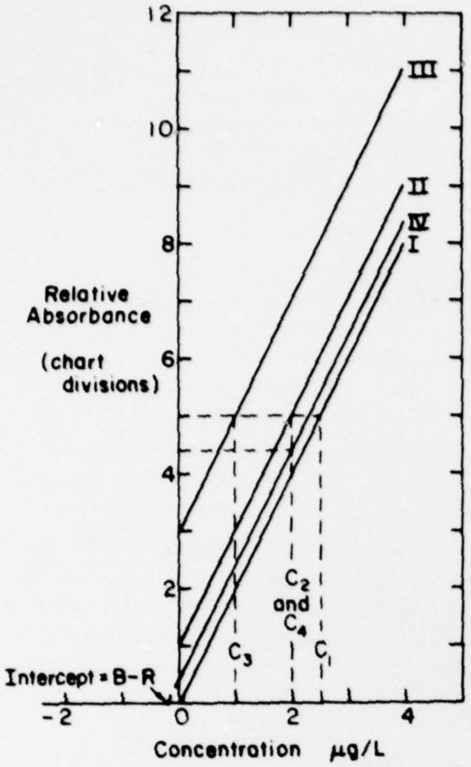

Figure 1. Theoretical calibration curves for standards containing various analyte impurity concentrations in the blank and in the reference distilled water. The slope for all curves is the same and is given by: slope = absorbance (div)/concentration (µg/l) = 2. The y intercept, however, varies with the impurity concentration of analyte in the blank (B) and in the reference (R) distilled water (curve I: B = 0, R = 0; curve II: B = 0.5 µg/l, R = 0; curve III: B = 1.5 µg/l, R = 0; and curve IV: B = 0.5 µg/l, R = 0.3 µg/l). As this figure shows, B raises the standards calibration curve while R lowers the curve. Sample S (see text) contains an actual (true) concentration of 2.5 µg/l in all cases. The x intercept (B–R) shown is for curve IV.

standards and samples are illustrated graphically in Figure 1 for four theoretical situations. In this figure, B is the concentration of analyte impurity in the DW used to prepare the standards and R is the concentration of analyte impurity in the reference DW used to zero the spectrophotometer.

Ideally, B = R = 0 (curve I) and the standards' calibration curve is a straight line passing through zero, so that actual sample concentrations can be found directly from the calibration curve. For example, a sample S that gives an absorbance of 5.0 chart divisions contains, from curve I, an analyte concentration of 2.5 µg/l (C_1).

If the DW used to prepare the standards contains 0.5 µg/l of analyte (curve II: B = 0.5 µg/l, R = 0), the actual analyte concentration of each of the standards will be 0.5 µg/l higher than expected and the corresponding absorbances will be high by 1.0 chart division. When these high absorbances for the standards are plotted vs the nominal or expected concentrations, the entire calibration curve is shifted upward by 1.0 division. In this instance, sample S, although still giving an absorbance of 5.0 chart divisions, will have an apparent concentration (C_2, from curve II) of only 2.0 µg/l. Correcting for B by adding 0.5 µg/l to the apparent sample concentration gives an actual concentration of 2.5 µg/l.

A higher concentration of analyte impurity in the DW used to prepare the standards simply shifts the calibration curve upward by a greater amount. Calibration curve III (B = 1.5 µg/l, R = 0) has moved upward 3.0 divisions due to a blank impurity concentration of 1.5 µg/l. Sample S, although still giving an absorbance of 5.0 divisions, will have an apparent concentration (C_3, from curve III) of only 1.0 µg/l. Correcting for B by adding 1.5 µg/l to this observed concentration gives the actual concentration of 2.5 µg/l.

The above three examples demonstrated the effect of B, the concentration of analyte impurity in the standards' DW, upon the calibration curve and samples. The reference DW was assumed to be free of analyte impurity (R = 0) which is usually not the case. The effect of R upon the standards is shown in curve IV where B = 0.5 µg/l and R = 0.3 µg/l. Comparing curve IV with curve II (B = 0.5 µg/l, R = 0) shows that if R = 0.3 µg/l the standards' calibration curve is shifted downward by 0.6 division. This downward shift due to R is distinct from the original upward shift of 1.0 division due to B = 0.5 µg/l, so that the net effect is an upward shift of the standards' calibration curve by 0.4 division. In addition, unlike B, which directly affects only the standards, R directly affects the absorbance of the samples as well as that of the standards. Since the sample also is analyzed vs R, the observed absorbance of sample S will now be 0.6 division low, or 4.4 (5.0 – 0.6) divisions. This sample, designated SI, contains (from curve IV) an apparent concentration C_4 of 2.0 µg/l. Correcting for B by adding 0.5 µg/l gives the actual sample concentration of 2.5 µg/l.

From the above, it can be seen that the value of R need not be known when analyzing samples because it equally affects absorbances of both standards and samples and is effectively cancelled out. Although the reference DW blank is traditionally called "the blank" in an analysis, its analyte concentration R does not affect sample concentrations. The actual blank correction added to samples is due to the analyte impurity in the standards' DW (B) and not due to that of the reference DW (R).

The preceding corrections are straightforward to apply if B is known. A precise method of determining B is to analyze an aliquot of the DW blank that has been concentrated several times by, for example, slow (nonboiling) evaporation in Teflon dishes. If flame AA is used and the blank is concentrated 10 times, the absorbance signal will be 10 times that of the blank signal. When this absorbance value is converted to an analyte concentration using the calibration curve, the observed concentration will be low by B because the standards forming the calibration curve are high by B. Thus, the observed concentration for a 10-fold concentrate is

$$\text{observed concentration} = 10B - B$$

and

$$B = \text{observed concentration}/9$$

or more generally

$$B = \text{observed concentration}/(CF - 1)$$

where CF is the blank concentration factor (number of times the blank was concentrated). Note that because the calibration standards contain B, the observed concentration is divided by CF − 1 and not simply by the concentration factor. The concentrated blank is treated as a sample and, as such, is corrected for B.

Another method that has often been used to determine B is extrapolation of the absorbance vs concentration calibration curve. The value of B is taken as the negative of the x axis intercept (absorbance = 0). However, as can be seen from Figure 1, this technique is valid only when $R = 0$, which is seldom the case. As shown for curve IV, the x axis intercept actually represents $B - R$. If $R = B$, then extrapolation will result in a value of zero for B, which again is incorrect. For analyses using flame AA, B cannot be reliably determined by extrapolation of the standards' calibration curve, but only by analysis of a concentrated blank.

Thus, for flame AA measurements the overall blank correction required is simply the addition of B, the concentration of analyte impurity in the distilled water used to prepare the standards, to all samples.

Flameless AA

Heavy metal samples analyzed by flameless AA (graphite atomizer) generally require three different blank corrections: 1) a "furnace blank," 2) a distilled water blank for the standards (B), and 3) an acid blank. These corrections should be applied in the order listed above.

The furnace blank is the absorbance signal obtained during atomization without a sample (i.e. an empty furnace). This baseline shift was first reported for Ca (Cragin and Herron 1973) and its magnitude depends upon the wavelength of the element being analyzed. Modification of the spectrophotometer optical system can significantly reduce the signal (Kerber et al. 1973) but does not completely eliminate it at high scale expansions. As a result, the furnace blank absorbance, when present, should be subtracted from all absorbance readings (blanks, standards, and samples) before any sample concentrations are made. In practice, correcting for furnace blank absorbance will not affect calculated sample concentrations since both standard and sample absorbances are affected equally. However, this correction is important if the standards' DW blank is determined by extrapolating the calibration curves back to the x axis intercept.

When using flameless AA, the concentration B of analyte in the standards' DW blank can be determined by one of two ways. The simplest method is by direct extrapolation of the standards' calibration curve. If this procedure is used, the calibration curve must first be corrected for the furnace blank by subtracting this absorbance signal from the absorbance of each of the standards (failure to do this will result in an erroneously high value for B). The value of B is then the negative of the x axis intercept (absorbance = 0) of the corrected absorbance vs concentration curve. This method is valid when using flameless AA because, unlike flame AA, a reference DW blank is not required to physically zero the instrument. The instrument can be zeroed on an empty furnace without atomization.

Another method to determine the value of B is to analyze preconcentrated blank aliquots, as described for flame AA measurements. Preconcentration can be performed either by evaporation in Teflon dishes or directly in the graphite furnace by sequentially drying multiple aliquots before atomization.

Once B has been found by either the extrapolation or the concentration method, its value should be added to all samples (including acid blanks).

The third correction usually required for flameless AA determinations of heavy metals is that due to the acid blank. A common method of preventing heavy metal loss from solution by adsorption onto container

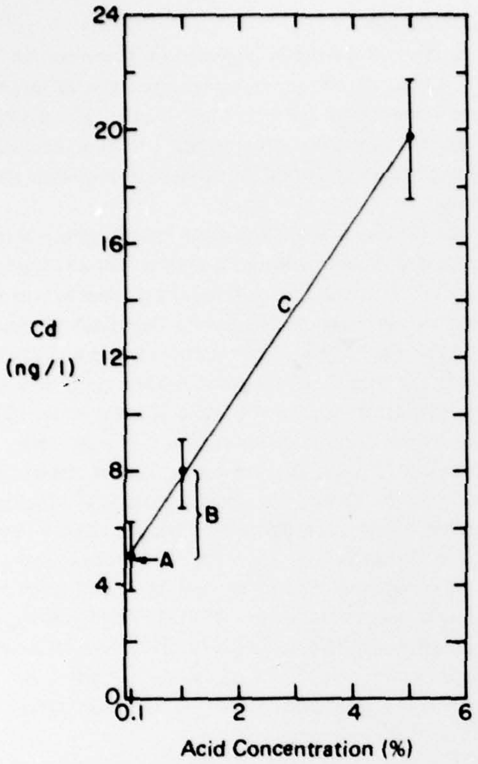

Figure 2. Experimentally determined concentrations of Cd in acid blanks of various acid concentrations in DDW. The plotted Cd concentrations, determined on 100-μl aliquots by flameless AA, have been corrected for the standards' DDW blank (3.7 ng Cd/l). The acid concentration is the volume proportion of concentrated (70%) HNO_3 in DDW (e.g. 1% represents 1:100 concentrated HNO_3 in DDW). In this figure, A = intercept = DDW Cd contribution to acid blank = 4.9 ng/l; B = 3.1 ng/l in 1% (1:100) acid; and C = slope = (19.6 – 4.9)/0.05 = 296 ng/l in concentrated acid or 3.0 ng/l in 1% (1:100) acid. Cadmium concentrations, found in this commercial high purity acid by either the slope or the blank subtraction method (0.30 and 0.31 μg Cd/l of concentrated acid), are well within the specifications of the manufacturer (< 1 μg Cd/l).

walls during storage is to acidify samples to a pH of 2 or less with HNO_3 or HCl. An acid blank, such as 1:100 (vol) concentrated acid in DW (1 ml of acid in 99 ml DW), is also prepared at the same time to determine the acid analyte impurity concentration for which the samples must be corrected. However, this acid blank contains analyte impurity not only from the acid (1% of the acid blank volume) but also from the DW (99% of the acid blank volume). (This DW is not necessarily the same as the DW used to prepare the standards.) Since the acidified samples contain acid and not DW, the contribution of the DW to the total acid blank impurity must be determined. Simply analyzing a separate unacidified aliquot of DW is not reliable because heavy metal loss by adsorption onto container walls during storage may result in erroneously low DW analyte concentrations. A more precise method of determining the acid and the DW analyte contributions to the acidified blank is to prepare and subsequently analyze a series of acid blanks in DW of different acid dilutions (vol), e.g. 1:20 (5%), 1:100 (1%), and 1:1000 (0.1%). A plot of the total observed analyte concentration (corrected for the standards' DW blank) in each of the acid blanks vs its acid dilution factor will be a straight line, the y intercept (x = acid concentration = 0) of which represents the analyte concentration in the DW used in the acid blank. Such a plot is shown in Figure 2 for experimentally measured concentrations of Cd in acid blanks of various dilutions with DDW. The analyte concentration in 1% (vol) (1:100) acid is then the difference between the total observed concentration in the 1% acid and the y intercept. For the example in Figure 2, this concentration is 8.0 – 4.9 = 3.1 ng/l.

Alternatively, the acid analyte concentration can be found directly from the plot of analyte concentration vs acid dilution without determining the acid DW blank. Since the slope of the line, 296 ng/l, is equal to the analyte concentration in pure undiluted acid the acid analyte contribution from the 1:100 acid blank will be equal to slope/100, or 3.0 ng/l, which agrees well with the 3.1 ng/l determined previously by the intercept-subtraction method. The slope method probably gives a somewhat more reliable figure since it is averaged over a wider concentration range. Regardless of which method is used, however, the value for the acid contribution should then be subtracted from all acidified samples (after correction for the standards' blank).

CONCLUSION

The absence of proper blank corrections in trace analysis leads to errors, positive or negative, which result in high or low apparent sample concentrations. Erroneously high sample concentrations will clearly result from failure to correct for an acid or reagent blank. Low sample concentrations can result not only from metal adsorption onto container walls but from failure to correct for the standards' distilled water blank. Hence, in an interlaboratory comparison of identical samples, the fact that one laboratory produces consistently lower values may not necessarily reflect superior contamination prevention procedures. The actual discrepancy may be due to analyte impurity in the distilled water blank, producing high standards and accordingly low observed sample concentrations.

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Cragin, James H.
Blank corrections for ultratrace atomic absorption analysis / by James H. Cragin and Steven T. Quarry. Hanover, N.H.: U.S. Cold Regions Research and Engineering Laboratory; Springfield, Va.: available from National Technical Information Service, 1979.
ii, 7 p., illus., 27 cm. (CRREL Report 79-3.)
Prepared for National Science Foundation by U.S. Army Cold Regions Research and Engineering Laboratory.
Bibliography: p. 5.
1. Acid blanks. 2. Adsorption. 3. Atomic absorption. 4. Blanks. 5. Heavy metals. 6. Spectrophotometry. 7. Standards. 8. Trace elements. I. Steven T. Quarry. II. United States. Army. Corps of Engineers. III. Army Cold Regions Research and Engineering Laboratory, Hanover, N.H. IV. Series: CRREL Report 79-3.

☆U.S. GOVERNMENT PRINTING OFFICE: 1979—600-802/319