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Using second-order calibration to identify and quantify aromatic sulfonates in water by high-performance liquid chromatography in the presence of coeluting interferences

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Abstract

We used the Generalized Rank Annihilation Method (GRAM), a second-order calibration method, to quantify aromatic sulfonates in water with high-performance liquid chromatography (HPLC) when interferences coeluted with the analytes of interest. With GRAM, we can quantify in only two chromatographic analyses, one for a calibration sample and one for the unknown sample. The calculated concentrations were not statistically different to those obtained when the chromatographic separation of the unknown sample was modified in order to completely separate the analyte from the interferences before univariate calibration. With GRAM, the concentrations are determined much more quickly because a complete resolution is not required.

Keywords: Generalized rank annihilation method; Chemometrics; Co-elution; Second-order calibration; Sulfonates

1. Introduction

Many factories discharge their wastewater into rivers or directly into the sea after a treatment process to eliminate the most common contaminants. In the tannery and dye industries, aromatic sulfonates are widely used and are highly soluble in water. They are difficult to remove completely by the treatment process and have been found in effluent waters [1]. Little is known about their toxicity but they have a low biodegradability, so they are potentially hazardous for the aquatic environment. It is therefore important to monitor them in these kinds of samples.

As the polarity of these compounds is high, the most common analytical technique is ion-pair liquid chromatography with UV–Vis or fluorescence detection [2,3]. This technique is not sensitive enough to quantify these compounds in real samples, so an enrichment step is needed before the chromatographic analysis. The most common preconcentration technique is ion-pair solid-phase extraction using highly crosslinked polymeric sorbents such as isolute ENV+, which has a high retention for the most polar analytes [1].

In natural waters, other polar compounds can also

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be retained in the solid-phase extraction process and coelute with the analytes of interest during the chromatographic analysis. This coelution may produce strongly biased quantifications when the concentration is determined with univariate calibration, which requires highly selective measurements. When coelution is detected, the conditions of the HPLC method must be optimized again from the unknown sample until the analyte of interest elutes separately from the interferences. This may be difficult if the properties of the analyte and interferences are similar and is an important outlay of time and resources. Also, since the interferences depend on the source of the sample, it may be cumbersome to optimize the conditions for each particular analyte and every unknown sample.

Mathematical separation is an alternative to chromatographic separation [4]. Diode array detectors (DAD) can record the UV–Vis spectra at every retention time, and a matrix (elution time× wavelength) is obtained for each peak to be quantified. Applying second-order calibration algorithms to this data matrix can: (a) indicate whether the peak of the analyte of interest contains coeluting interferences, (b) determine the number of coeluting species, (c) determine which species are present on the basis of their spectral features—qualitative analysis—and (d) determine the concentration of the analyte of interest in the overlapping peaks (known as the ''second order'' advantage) [5].

Of the second-order calibration algorithms that allow quantification in the presence of non-calibrated components, the Generalized Rank Annihilation Method (GRAM) [6] is very useful for chromatographic data, where the number of analyses is important. It only requires two data matrices. One of these is from a calibration sample, i.e. the spectra measured at the different retention times of the peak of the analyte obtained by analyzing either a pure standard or a sample with a known added concentration of the analyte. The other is the spectra measured at the different retention times of the peak from the unknown sample. Moreover, GRAM has been widely studied [7–14] and mathematical expressions are available for calculating figures of merit [15] and the variance of the predicted concentrations [16].

In its application to HPLC–DAD data, it was pointed out that the different elution times of the analytes of interest between analysis is an important problem that leads to misleading results [13]. For this reason, the application of GRAM to experimental chromatographic data in routine analysis is not as straightforward. Here we report a systematic methodology for routine quantification using GRAM. This includes a previous time shift correction step with a recently developed algorithm [17] that allows a selective correction of the time shift depending on the analyte of interest.

This methodology was applied to an implemented in-house routine method for the determination of six aromatic sulfonates. When analyzing a sample of water from a sewage treatment plant in Tarragona (Spain), the peak of two of the analytes of interest overlapped with interferences. While the other four could be determined by univariate calibration, the quantification of the two other analytes required modifying the separation conditions until the peaks were completely resolved. This paper shows that it is possible to quantify the unresolved peaks with GRAM without more experimental work. Statistical tests are used to assess that the concentrations found by both GRAM and full resolution of the peaks are comparable.

2. Theory

This section briefly describes the chemometrical tools we have used in this paper. There is a more detailed explanation of the algorithms in the cited references.

We will use these conventions: bold uppercase letters to indicate matrices, e.g. **A**; italic lowercase letters to indicate scalars, e.g. *a*; and superscript T to indicate transposition.

For every analyzed sample, the peak of the analyte of interest (either pure or overlapped with interference) is represented by a matrix **R** (time× wavelength), where the element r_{ij} represents the absorption measured at the *i*th retention time and the *j*th wavelength.

2.1. Generalized Rank Annihilation Method (GRAM)

For GRAM, the calibration matrix ($\mathbf{R}_o$) is the spectra at each retention time of the peak of the

analyte obtained by analyzing the pure standard. The concentration of the analyte of interest ($c_{o,k}$) is known. The prediction matrix is the spectra at each retention time of the peak of the analyte in the unknown sample ($\mathbf{R}_u$). Both matrices are the same size ($J_1 \times J_2$) and it is assumed that they can be expressed as:

$$\mathbf{R}_o = \mathbf{X}\mathbf{C}_o\mathbf{Y}^T + \mathbf{E}_o$$

$$\mathbf{R}_u = \mathbf{X}\mathbf{C}_u\mathbf{Y}^T + \mathbf{E}_u$$

where $\mathbf{X}$ ($J_1 \times K$) and $\mathbf{Y}$ ($J_2 \times K$) contain the normalized chromatographic profiles and spectra, respectively, K is the total number of analytes in both matrices, $\mathbf{C}_o$ and $\mathbf{C}_u$ are $K \times K$ diagonal matrices of concentration related scale factors, and $\mathbf{E}_o$ and $\mathbf{E}_u$ are $J_1 \times J_2$ error matrices. Calibration and prediction with GRAM is a four-step process [16]:

1. Singular value decomposition of the matrix $\mathbf{Q} = \mathbf{R}_u + \mathbf{R}_o$ as $\mathbf{Q} = \mathbf{U}\mathbf{S}\mathbf{V}^T + \mathbf{E}$. This equation is calculated only for a number of factors equal to the total number of analytes contained in both matrices.
2. Resolution of the eigenvalue problem $(\mathbf{S}^{-1}\mathbf{U}^T\mathbf{R}_u\mathbf{V})^T\mathbf{T} = \mathbf{T}\mathbf{\Pi}$, where the diagonal elements of $\mathbf{\Pi}$ are the eigenvalues π_k and $\mathbf{T}$ is the matrix of eigenvectors.
3. Calculation of the chromatographic profiles (peak shapes) $\mathbf{X} = \mathbf{U}\mathbf{\Pi}\mathbf{T}$ and the pure spectra $\mathbf{Y} = \mathbf{V}(\mathbf{T}^{-1})^T$.
4. Calculation of the concentration of the analyte k in the unknown sample:

$$c_{u,k} = \frac{c_{o,k}\pi_k}{1 - \pi_k}$$

In Step 4, we need to assign which of the calculated eigenvalues corresponds to the analyte of interest. We do this by calculating the correlation coefficient between the spectrum of the pure analyte (available from the peak of the pure standard) and the spectrum calculated with GRAM in $\mathbf{Y}$. The eigenvalue associated with the spectrum with the highest correlation is used for prediction in step 4.

2.2. Time shift correction for the unknown sample peak

One requirement that prevents GRAM from being used in routine chromatographic analysis is that the data matrices containing the peak of the analyte in the calibration sample and in the unknown sample must be trilinear [10,18]. This means that the chromatographic profile of the analyte in the unknown sample must have the same shape and elute at the same time as in the calibration sample matrix. Of these two requirements, complete coincidence of retention time is not common in practice, because imprecision in injection timing, fluctuation in temperature, and changes in flow-rate introduce time shifts in the peaks. The characteristics of ion-pair chromatography also largely influence the time shift. Several approaches exist for solving the problem of the time shift in different chromatographic runs [14,19] and improve trilinearity. We applied a recently developed time shift correction algorithm to $\mathbf{R}_u$ before we applied GRAM [17].

The algorithm used is based on selecting the correct time window for $\mathbf{R}_u$. Both $\mathbf{R}_o$ and $\mathbf{R}_u$ are individually decomposed into pure spectra and concentration profiles using Iterative Target Transformation Factor Analysis (ITTFA) [20–22]. The peak of the analyte of interest in both matrices is located and a time window for $\mathbf{R}_u$ is selected so that both matrices are aligned with respect to the analyte of interest. This alignment is made so that the maximum of the profile of the analyte of interest in both matrices occurs at the same time. To apply GRAM, $\mathbf{R}_o$ and $\mathbf{R}_u$ must have the same number of rows (time units) and columns (wavelengths). However, to correct the time shift, $\mathbf{R}_u$ is first selected at a wider time window than the calibration matrix to ensure that the profile of the analyte is contained in the selected window. Using this methodology the matrices are selectively aligned with regard to the analyte of interest.

3. Experimental

3.1. Reagents, standards and samples

3-Amino-1-benzenesulfonate, 6-amino-4-hydroxy-2-naphthalenesulfonate, 6-amino-1-hydroxy-3-naphthalenesulfonate, 1-amino-6-naphthalenesulfonate, 1-naphthalenesulfonate and 2-naphthalenesulfonate were obtained as free acids or sodium salts from Fluka (Buchs, Switzerland) or Aldrich Chemie

(Beerse, Belgium). Standard solutions of 1000 mg l^{-1} of each compound were prepared in Milli-Q quality water. To increase solubility, we added several drops of sodium hydroxide 0.1 N. All samples used in this study were prepared from these solutions.

We used disodium hydrogen phosphate (Panreac, Barcelona, Spain), sodium dihydrogen phosphate (Probus, Badalona, Spain), phosphoric acid 85% (Probus, Badalona, Spain), tetrabutylammonium bromide (Fluka, Buchs, Switzerland), methanol (HPLC grade, SDS, Peypen, France) and acetonitrile (HPLC gradient grade, SDS, Peypen, France) to prepare mobile phase and samples.

Samples were collected from the output of the sewage treatment plant in Tarragona (Spain) in precleaned amber glass bottles, filtered through a 0.45-μm membrane filter and kept at 4 °C until analysis. Although the 6-amino-1-hydroxy-3-naphthalenesulfonate (A) and the 1-amino-6-naphthalenesulfonate (B) had been previously found [1] in this kind of wastewater, they were not present in the analyzed sample. Therefore, the samples were spiked at 0.08 and 0.15 mg l^{-1} to ensure their presence and test the usefulness of GRAM.

3.2. Instrumental

Chromatographic analyses were carried out using an HP1100 series system (Agilent Technologies, Waldbronn, Germany) equipped with a Rheodyne manual injector with a 20-μl injection loop, a degasser, a binary pump, a column oven and a diode-array detector. The chromatographic column was a 25.0 cm × 0.46 cm Kromasil 100 C_{18} with a 5-μm particle size (Teknokroma, Barcelona, Spain).

The enrichment was carried out using a solid-phase extraction manifold (Teknokroma, Barcelona, Spain) connected to a vacuum pump (Gast Manufacturing Company, Buckinghamshire, UK).

3.3. Experimental conditions

3.3.1. Chromatographic conditions

3.3.1.1. Conditions 1

These conditions correspond to the in-house implemented method optimized for the determination of the six aromatic sulfonates indicated in the Reagents, standards and samples section. The optimal separation of a standard sample containing the six aromatic sulfonates was carried out under isocratic conditions at 30 °C with a flow-rate of 1 ml min^{-1}. The aqueous component of the mobile phase was a Milli-Q water solution containing 8 m*M* of disodium hydrogen phosphate, 8 m*M* of sodium dihydrogen phosphate and 7 m*M* of tetrabutylammonium bromide. Its pH was adjusted to 6.5 with phosphoric acid and the resulting solution was filtered through a 0.45-μm membrane filter [2]. The organic component was acetonitrile (30%). The spectra from the effluent of the chromatographic system were recorded between 220 and 300 nm, every 0.4 nm. The spectra were recorded every 0.4 s. The analysis lasted 17 min.

When we analyzed the wastewater sample, the 6-amino-1-hydroxy-3-naphthalenesulfonate (A) and the 1-amino-6-naphthalenesulfonate (B) eluted overlapped with other interferences, so we concentrated specifically on quantifying these two analytes.

3.3.1.2. Conditions 2

These conditions were determined for the wastewater sample in order to fully separate the analytes A and B that, in Conditions 1, overlapped with interferences. In this case, the optimal composition of the mobile phase was 22% acetonitrile and the chromatographic separation lasted 65 min. Absorbance was measured at 250 nm because this wavelength was selective for the analytes of interest.

3.3.2. Solid-phase extraction

Before solid-phase extraction, tetrabutylammonium bromide was added to the sample in a concentration of 3 m*M* as an ion-pairing reagent and the pH was adjusted to 7 with a disodium hydrogen phosphate/sodium dihydrogen phosphate buffer to ensure the ion-pair formation. The preconcentration cartridge, an Isolute ENV+ cartridge (International Sorbent Technology, Mid. Glamorgan, UK), was conditioned with 5 ml of acetonitrile and 5 ml of Milli-Q water. Then 50 ml of sample was preconcentrated at a flow-rate of 5 ml min^{-1}. Finally, the retained analytes were eluted with 5 ml of methanol. Solvent was eliminated with a nitrogen carrier stream and the analytes were redissolved with 1 ml of the

chromatographic mobile phase. In these conditions, recoveries (of the six aromatic sulfonates) were between 50 and 90%, with %RSD between 4 and 8%.

3.4. Software

All calculations were done using in-house subroutines for MATLAB [23] version 6.

4. Results and discussion

4.1. Detection of overlap

Fig. 1 shows the superposed chromatographic profiles recorded from 220 to 300 nm of the wastewater spiked at 0.08 ppm of A and B. The vertical lines indicate the expected elution time of A and B that had been found with standards. Overlap of the peaks of these analytes was detected by visual inspection of the spectra over time and calculation of the chemical rank for each peak. A closer look at the peaks reveals that they are time shifted with respect of the peaks from the standards. Fig. 2a shows the profile of A obtained from the pure standard of 0.4 ppm of A ($\mathbf{R}_o$). Fig. 2b shows the peak of analyte A overlapping with other interferences in the wastewater sample analysis, which was later used for prediction with GRAM. No selective wavelengths were found, so quantification using univariate calibration may be largely biased. With conditions 1, we used the GRAM to determine the concentration of A and B.

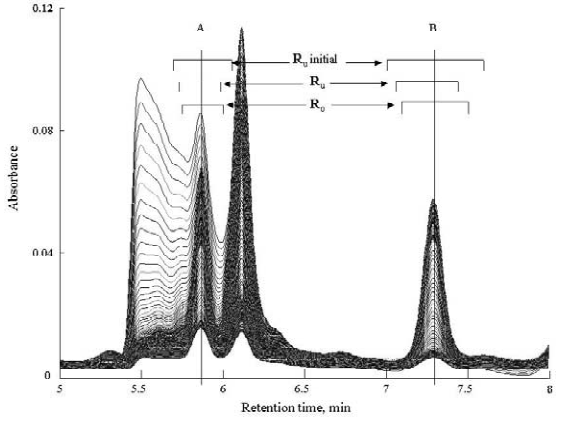

Fig. 1. Superposed chromatographic profiles of the wastewater recorded from 220 to 300 nm spiked with 0.08 ppm of A and B from 5 to 8 min. The vertical lines indicate the expected elution time for both analytes determined with standards. The time windows selected for $\mathbf{R}_o$ and $\mathbf{R}_u$ (before and after time-shift correction) are indicated.

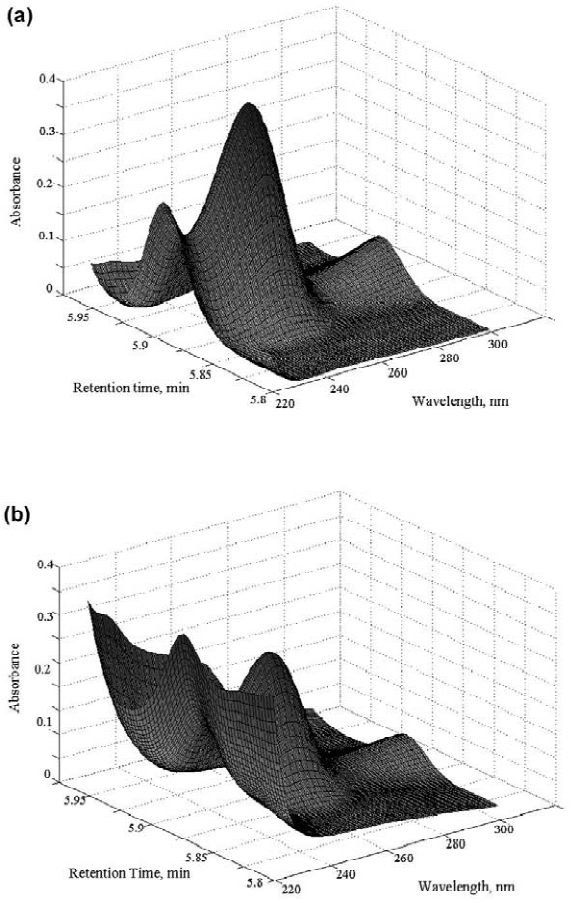

Fig. 2. Peak of analyte A in the wavelength range studied. (a) A pure standard of A. (b) Wastewater, where A elutes overlapping with interferences.

4.2. Time shift correction and GRAM

For the calibration matrices $\mathbf{R}_o$, we considered the time window where each analyte elutes. In this case, it was from 5.75 to 6.01 min for A and from 7.10 to 7.52 min for B. To correct the time shift in the wastewater sample, we selected a window that was 10 time steps wider on both sides, i.e. from 5.68 to

6.07 min for A and from 7.03 to 7.59 min for B. Fig. 1 schematically shows the time windows of $\mathbf{R}_o$ and $\mathbf{R}_u$ before and after we applied the time shift correction. Notice that for applying GRAM, the time window for $\mathbf{R}_u$ was the same size as $\mathbf{R}_o$.

In all cases, we calculated GRAM with two factors. Fig. 3 compares the spectra calculated by GRAM when determining A using the same time window for both matrices, i.e. not taking into account the time shift, and the spectra calculated by GRAM once the time shift was corrected. The calculated spectra of analyte A are very similar in both cases. The correlation coefficients of the spectrum of A in the pure standard and both calculated spectra were higher than 0.996. However, the shape of the spectrum of the interference was like that obtained in the non-spiked water only when the time shift was corrected. Results were similar for analyte B, whose correlation coefficient between the GRAM calculated spectrum of B and the spectrum of B measured in a standard sample, was higher than 0.999. If GRAM was applied without a correction of the time shift, considering the same time window for $\mathbf{R}_o$ and for $\mathbf{R}_u$, large prediction errors, around 30% were obtained.

In the initially optimised conditions 1, we recorded three replicate data matrices for the calibration sample (the standard contained 0.4 ppm of A and 0.4 ppm of B) and three for the unknown sample. Therefore, we were able to calculate nine different GRAM models (after the time shift had been corrected) by combining each calibration and each unknown sample matrix at each spiked level. To calculate the mean concentration and the precision (expressed as standard deviation) of the method, the nine models were divided into three groups of three models each, as shown in Table 1. All the models in each group are independent, since no matrix is repeated. From each group, the mean and the standard deviation of the predicted concentration are calculated. A pooled variance [24] was calculated as:

$$s^2 = \frac{\sum_i (n_i - 1)s_i^2}{\sum (n_i - 1)}$$

where $n_i = 3$ is the number of elements in each group. The denominator corresponds to the degrees of freedom that were used in the statistical test (see next section). In this case there were six degrees of freedom. As an example, Table 1 contains the results for analyte A in the sample spiked at 0.08 ppm.

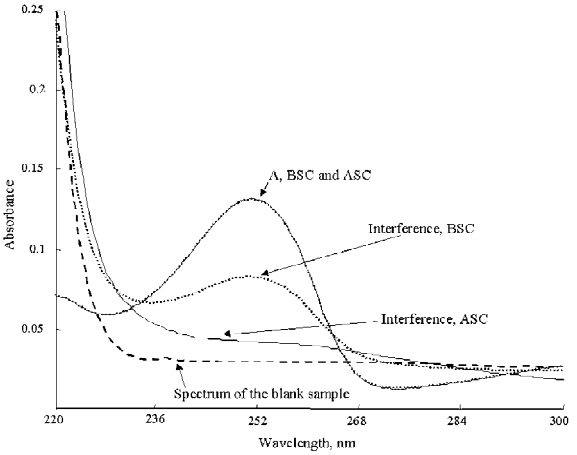

Fig. 3. Calculated spectra with GRAM in the determination of analyte A. (· · ·) Before shift correction (BSC) of $\mathbf{R}_u$; (—) after shift correction (ASC) of $\mathbf{R}_u$; (- - -) spectrum of a blank sample, where analyte A was not present.

4.3. Validation

We compared the predicted concentration values obtained by GRAM with the values obtained by univariate calibration. The experimental conditions were again optimized for the water sample so that analytes A and B eluted separately from any interfer-

Table 1
Mean value and standard deviation of the GRAM models for the analyte A spiked at 0.08 ppm

	Group 1	Group 2	Group 3
$\mathbf{R}_o/\mathbf{R}_u$	1–I	1–II	1–III
	2–II	2–III	2–I
	3–III	3–I	3–II
Mean concentration	0.0650	0.0648	0.0650
Standard deviation (s_i)	0.0059	0.0006	0.0052
Grand mean (calculated concentration)		0.065	
Standard deviation		0.003	

Three groups of three independent models were analyzed, combining each calibration $\mathbf{R}_o$ (1,2,3) and prediction $\mathbf{R}_u$ (I, II, III) matrices.

ence. Under these conditions 2, which we have specified in the Chromatographic conditions section, the test sample was measured three times. We carried out univariate calibration at 250 nm using standard solutions of A and B with concentrations ranging from 0 to 0.2 ppm. Linearity was very acceptable for this range, with determination coefficients (R^2) of 0.9984 and 0.9990 for A and B, respectively.

Table 2 shows the predicted concentration values obtained by GRAM and the values obtained by univariate calibration. An *F*-test was used to evaluate the precision of both methodologies. With a confidence interval of 95%, no significant differences were observed, i.e. at this level of significance, both strategies provide the same precision.

We used a two-sided *t*-test to compare the results obtained with GRAM with those obtained with univariate calibration. This comparison was not carried out using the value of the initial spiked concentration in order to avoid errors due to the irreproducibility of the extraction and chromatographic processes.

In all cases, the results were similar for a confidence interval of 95%. This proves that, for the studied cases, GRAM can be used for quantification and that the results obtained with this method are similar to those obtained with univariate calibration. It is important to note that the peaks of the analytes A and B eluted in less than 8 min. In this case, their shapes were sufficiently similar among the different samples to enable good quantification. Nevertheless, in future applications of GRAM, it must be considered that if the analyte of interest elutes at much higher retention times, the shape of its chromatographic profile may vary from one sample to another, causing a significant deviation from the trilinearity and unreliable predictions. Usually, this can be detected by comparing the spectrum calculated by GRAM and the spectrum of the pure standard.

5. Conclusions

We have shown that GRAM can be used to quantify aromatic sulfonates in environmental samples with HPLC–DAD when the peak of the analyte of interest is not completely resolved from the other interferences. As it requires only two analyses, GRAM is an efficient alternative to the tedious and time-consuming chromatographic separation of the analytes followed by univariate calibration. The problem of time shift between the calibration and the unknown sample in GRAM can be solved, and results are similar to univariate calibration. GRAM can be applied to samples from different sources without any extra experimental work. With univariate calibration, optimization must be done for each individual analyte in every sample, which in practice is almost impossible.

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Table 2
Mean concentration and standard deviation obtained by GRAM and univariate calibration for analytes A and B spiked at two concentration levels

Analyte	Spiked concentration (ppm)	GRAM (conditions 1)		Univariate calibration (conditions 2)		*t*-Test	
		Calculated concentration	Standard deviation	Calculated concentration	Standard deviation	Calculated	Minimal alpha (%)
A	0.08	0.065	0.003	0.065	0.005	0.01	62
A	0.15	0.167	0.007	0.173	0.005	1.09	77
B	0.08	0.084	0.003	0.089	0.002	2.05	95
B	0.15	0.171	0.005	0.166	0.003	1.35	84

t-Test indicates the calculated *t*-value and the minimal alpha so that $t_{\text{calculated}} < t_{\text{tabulated}}$.

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