SODIUM BENZOATE ANALYSIS
FOR ON-LINE BRINE FLOW MEASUREMENTS

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Abstract

The optimum conditions for the analysis of sodium benzoate in brine matrix using the Shimadzu HPLC system were determined. This system is composed of a single-pump, an on-line degasser, an auto injector, an oven, a UV detector and an ODS reverse-phase column. This was done in order to develop an accurate, precise, and fast method for the analysis of sodium benzoate, a chemical tracer for on-line brine jlow measurements.

Isocratic runs using methanol-phosphate buffer eluent of 55:45 v/v ratio and 1.0 mL/minute flow rate at 230 nm wavelength was found to give very good results in terms of baseline stability, freedom from interference and speed of analysis. Benzoate retention time at this conditions is 2.8 minutes. Linearity of the instrument response within the range of at least 0.05 ppm to 200 ppm benzoate, for a 5 μL sample injection has been established. Accuracy of more than 99 % has been consistently obtained for both benzoate standards and actual tracer samples. Precision is very high with an established COV of the method of <1 %. Matrix interference is found to be very minimal.

Benzoate is found prone to degradation due to microbial action. This however, can be controlled by acid treatment, addition of sodium azide solution, or refrigeration.

1.0 INTRODUCTION

PNOC-EDC recently adapted a new system for on-line determination of bore-output from Thermochem, Inc. which is capable of doing simultaneous injection of steam-phase and water-phase tracer chemicals into a well, a method known as Tracer Flow Test (TFT). Steam and water flow are determined based on changes in the concentration of tracer chemicals as they are diluted by the flowing fluid. The concentrations of the tracer chemicals before and after injection as well as the known injection rates are used for calculating the steam flow, the water flow and eventually the enthalpy of the well. Chemical tracer for steam flow measurement is sulfur hexafluoride (SF_6) gas while tracer for water flow determination is sodium benzoate.

Thermochem uses a Dionex ion-chromatograph with an ion-exchange column and acetonitrile-sodium chloride eluent (gradient) for their sodium benzoate analysis. PNOC on the other hand has a Shimadzu HPLC unit with a C-18 reverse phase column which was yet to be tested for the analysis of benzoate in brine. The need to develop an appropriate analytical method for the analysis of sodium benzoate in brine matrix using the Shimadzu HPLC system has therefore become imperative.

This paper summarizes the results of the testing and method development for benzoate analysis in brine matrix conducted at the LGPP laboratory using the Shimadzu HPLC unit. This study has the following objectives:

- To develop an appropriate method for the analysis of benzoate in brine using the Shimadzu HPLC system.
- To establish the instrument detection limit. linear dynamic range. precision and accuracy.
- To determine the effect of brine matrix on sodium benzoate
- To determine the most suitable sample treatment for benzoate in brine.
- To establish sodium benzoate holding time.

2.0 INSTRUMENT OPERATING PARAMETERS

Tabulated below **are** the instrument operating parameters used during the tests:

Instrument	Shimadzu HIC 10Ai
Column	STR-ODS (C-18)
Mobile phase	methanol-phosphate buffer (10 mM)
	acetonitrile-sodium chloride
Flow Rate	0.8 mL/minute
	10 mL/minute
Detector	UV
Wavelength	230
Oven temperature	40 °C

The **Shimadzu** HPLC system is composed of the following units: a solvent delivery module which can handle up to four solvents, an on-line resin membrane degasser, a quaternary pump. an auto-injector, **an** oven, and a W detector. The system is interfaced with a computer-based chem-station which controls individual units and handles **peak area** integration and calculations of concentrations. Refer to Figure 1 for the instrument schematic diagram.

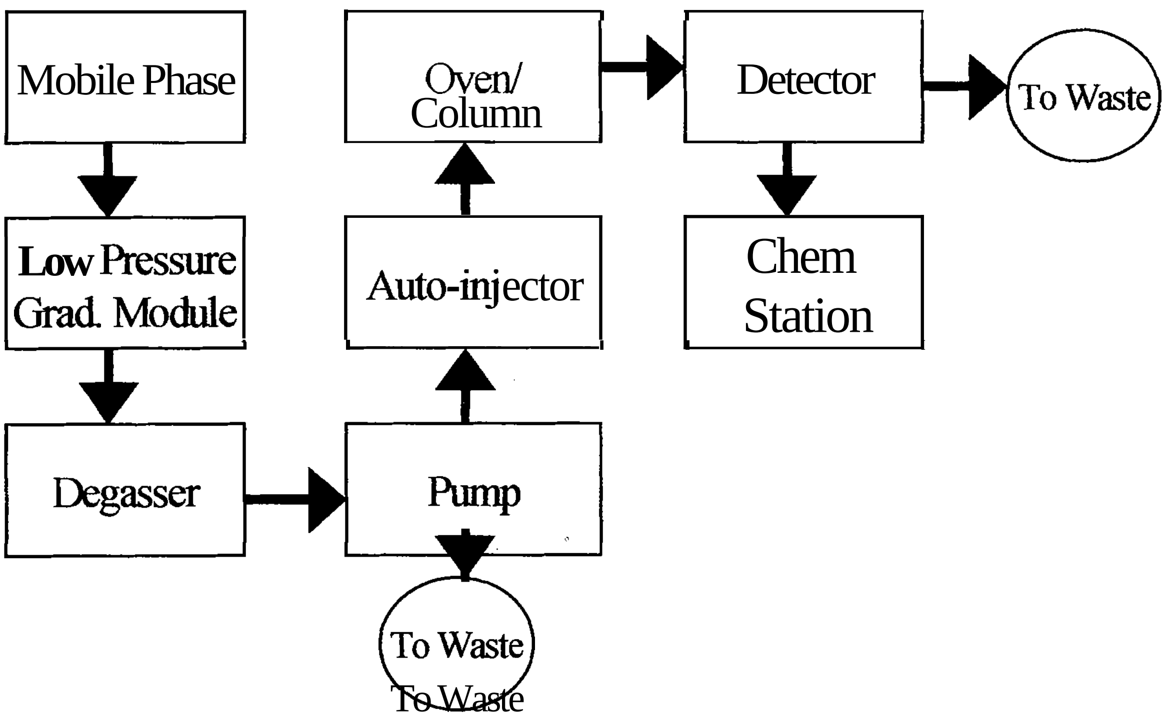

Figure 1. Schematic **Diagram** Of The HPLC

3.0. RESULTS AND DISCUSSION

3.1 Effect of Mobile Phase on Benzoate

The mobile phase plays a very important role in HPLC analysis because aside from serving as carrier of the sample, it also affects the chromatogram baseline, the quality of separation of the target peak from interfering peaks, as well as the retention time of the peaks.

Figure **2** shows the chromatogram of a run using acetonitrile-sodium chloride-water eluent **(25:5:70** v/v, isocratic), at **0.8mL/minute** flow rate. This mobile phase is adjusted to basic pH with NaOH where sodium benzoate exists as benzoate ion. Benzoate standards tested ranged from 0.01 to **5.00** ppm. This mobile phase appears to be not very suitable for benzoate analysis as shown by the dips in the baseline right before and after benzoate peak. For this chromatogram, peak area integration would include the area bounded by the dips and the original declared baseline accounting for positive error. Although it is possible to force a baseline so as not to include this portion, each chromatogram has to be processed individually to account for slight variations in peak width and retention time, consequently, defeating the purpose of automation. The presence of this negative peaks was observed for all concentration levels of benzoate standard tested. A large peak can also be seen eluting close to the benzoate peak. These results indicate that this mobile phase is not very suitable for the C-18 reverse-phase column. The analytical column of the Dionex system of Thermochem, which uses this mobile phase, separates though ion-exchange and is perhaps more suitable for this type of eluent.

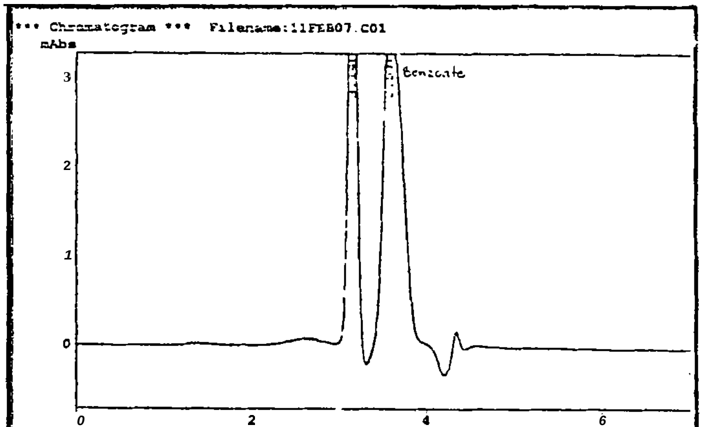

Figure *2* **Sodium** Benzoate Run With CH_3CN-NaCl-H_2O (25:5:70 v/v) at 0.8 mL/min **Flow**

The same samples were analyzed using methanol - phosphate buffer, 10mM (50:50 v/v, isocratic) eluent at a flow rate of 0.8 mL/minute. This solvent has a pH of ~ 3 where benzoate exists as benzoic acid. From the chromatogram shown in Figure 3, it *can* be observed that baseline is very stable and no dips *can* be noticed right before and after benzoate peak. Elution time of benzoate is **5.4** minutes. Minor peaks are also detected but are completely resolved from the benzoate *peak*. The negative peak seen at around **2** minutes is called a "water dip" which is a manifestation of the solvent front.

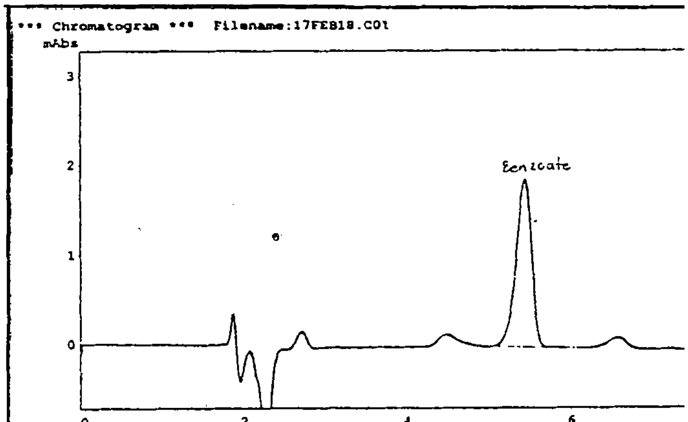

Figure 3. Sodium Benzoate Run With Methanol–Phosphate Buffer **(50:50** v/v, **isocratic) at** 0.8 mL/min Flow

This solvent was made slightly less polar by increasing the methanol-phosphate buffer ratio to 55:45. The flow rate was also increased to 1.0 mL/minute. **This has** decreased benzoate arrivaltimefrom **5.4** minutes to 2.8 minutes with no notable decline in baseline stability **and peak** separation (Fig. 4). These results indicate that methanol-phosphate buffer is a very appropriate mobile phase for the analysis of benzoate in brine in terms of baseline stability, freedom fiom interference and speed of analysis.

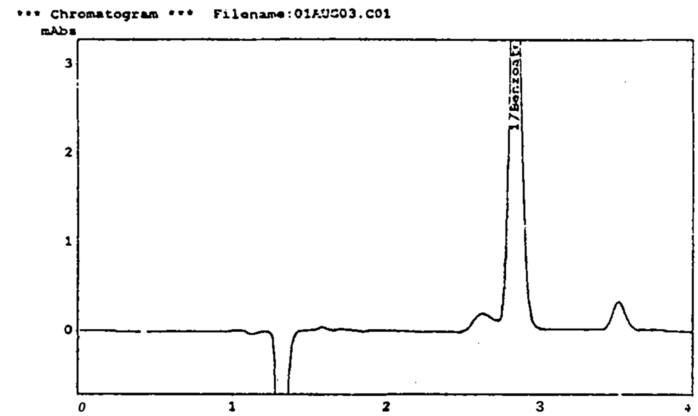

Figure 4. Sodium Benzoate **Run** With Methanol-Phosphate Buffer(55:45 v/v, isocratic)**at** 1.0mL/min Flow

3.2 Effect of Matrix on Benzoate,

Initial testing of **sodium** benzoate in brine shows that the benzoate **peak** elutes on the tail of a very large peak, initially ***suspected*** to be either chloride or silica. However, tests have confirmed that the large **peak** is nitrate ion **from** the nitric acid whch was added on the brine during sample collection, a standard sampling **procedure** in **LGPP.** Runs of benzoate **standards spiked** on freshly collected and untreated brine are shown below.

Table 1. Analysis of 1 ppm benzoate in brine

Sample	Concn. (Calc.)	Concn. (Analyzed)			Mean	SD	COV	% Recovery
		1	2	3				
MAH-289	1.00	1.02	1.03	1.00	1.02	0.03	1.43	101.75
108-683	1.00	1.00	0.99	1.00	1.00	0.00	0.23	99.47
105-544	1.00	1.00	1.00	1.02	1.00	0.01	1.11	100.51
106-634	1.00	1.02	1.00	1.00	1.00	0.01	0.84	100.47

Results show very high recovery for four **brine** samples ranging **fiom *99.5%*** to 101.8%. **Very high** agreement between replicates **was** also noted with COV ranging from 0.23 - 1.43%. **This** indicates that **matrix** effect on benzoate is very **minimal.**

Table 2. Effect of dilution on benzoate in brine

Sample	Dilution	ppm Benzoate			SD	COV	% Diff.
		1	2	Mean			
W306-4	0X	65.46	65.57	65.52	0.08	0.12	0.00
W306-4	2X	65.75	65.7	65.73	0.04	0.05	-0.32
W306-4	5X	65.35	65.53	65.44	0.13	0.19	0.11
W306-4	10X	64.22	64.37	64.30	0.11	0.16	1.86

The effect of dilution on benzoate was also done to **further** explore the effect of **matrix** on brine. Spiked brine samples were diluted up to 10 times and analyzed for benzoate. Results **are shown** in Table 2.

Figure 5 shows the absorbance spectrum of benzoic acid. Benzoate ion, being injected into a **steam** of acidic eluent (pH~3.0), is converted to benzoic acid and is analyzed as such. Sample analysis is done *at* 230 nm which corresponds to the most sensitive wavelength. Runs were made at this wavelength using a **5** µL injection volume at benzoate concentrations of 0.05 ppm, 0.10 ppm, *0.50* ppm, 1.00 ppm, and 2.00 ppm. A plot of instrument response to concentration was made and is shown in Figure 6. Instrument response is linear from concentration as low as 0.05 ppm (50 ppb) up to 2.0 ppm with correlation coefficient of 0.9998. **This** implies that concentrations as low as 0.01 ppm can be detected by using higher injection volumes (e.g. 25 µL or higher).

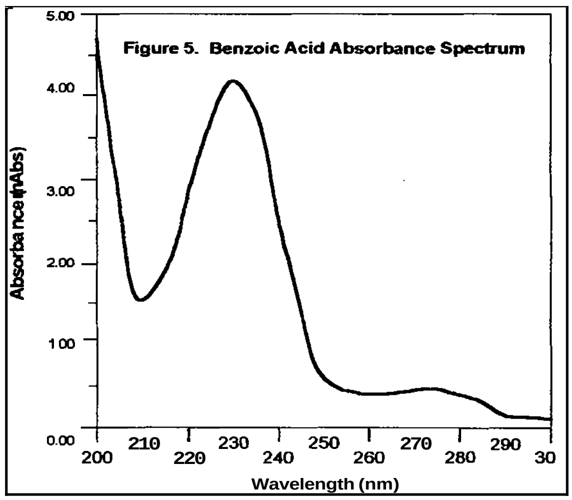

Figure 5. Benzoic Acid Absorbance Spectrum

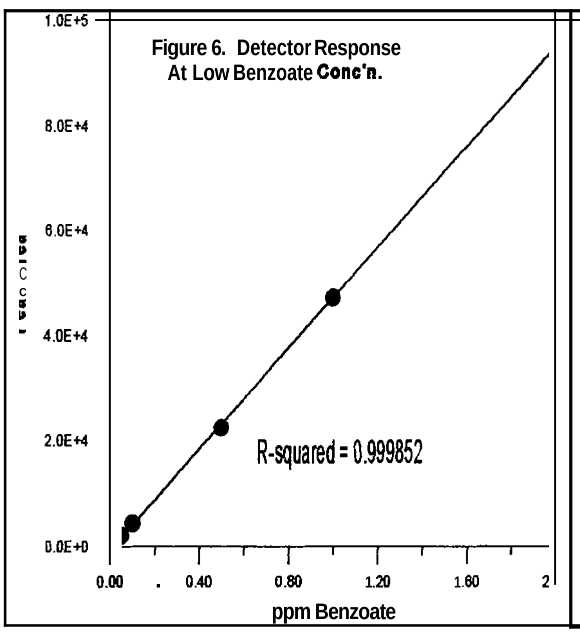

Figure 6. Detector Response At Low Benzoate Conc'n.

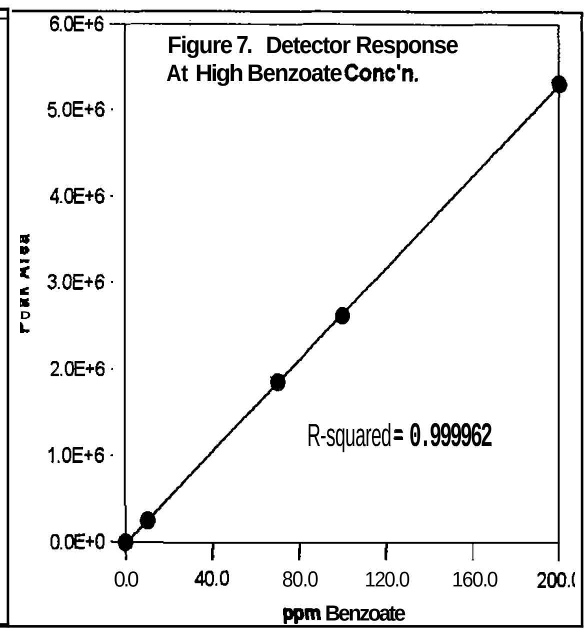

Figure 7. Detector Response At High Benzoate Conc'n.

3.4 Method Precision and Accuracy

Table 3. Analytical Precision For Sodium Benzoate

Sample Type	No. Of Runs	Mean Conc'n.	SD	COV	+/-	
					ppm	%
Standard	5	1.0	0.01	0.70	0.01	0.90
Standard	5	9.9	0.01	0.08	0.01	0.09
Standard	5	20.2	0.07	0.34	0.09	0.42
Brine	8	12.6	0.10	0.76	0.08	0.66
Brine	7	19.7	0.19	0.98	0.18	0.91
Brine	5	57.0	0.17	0.30	0.21	0.37
Brine	5	58.1	0.16	0.28	0.20	0.34
Brine	5	188.4	0.36	0.19	0.45	0.24

Analytical precision was determined by doing multiple analysis of benzoate standards and actual tracer samples. The confidence interval (+/-) at 95% confidence limit was established using equation 1.

Confidence interval (+/-) = $ts / n^{1/2}$ *equation 1.*
where t = statistical t factor

Sample Type	No. Of Runs	ppm Benzoate		SD	COV	Accuracy (%)
		Theo.	Anal.			
Standard	21	50.0	49.9	0.47	0.94	99.7

Results are obtained from 21 separate batches of analysis done on a 50.0 ppm external control sample. Mean concentration is 49.9 ppm which translates to an accuracy of 99.7 % The method can therefore be relied to deliver results with greater than 99% accuracy.

3.5 Sample Treatment and Benzoate Holding Time

One of the problems in the analysis of benzoate is the very **high** content of silica in LGPP brine samples which normally ranges from 600 - *800* ppm. Polymerized silica clogs the **0.45** µm filter membrane used to clean the samples making it very difficult to complete the filtration process. The possible occlusion of benzoate ions in the network of polymerized silica is also a concern. To address ***this***, sample treatment with acid as well **as** dilution was tested to determine their effect on benzoate analysis and on benzoate storage life. Of the acids tested (HCl, H_2SO_4, and HNO_3), nitric acid was found inappropriate for sample treatment due to the presence of nitrate ion whch has a strong absorbance at 230 **nm**. HCl and H_2SO_4 were found to have no

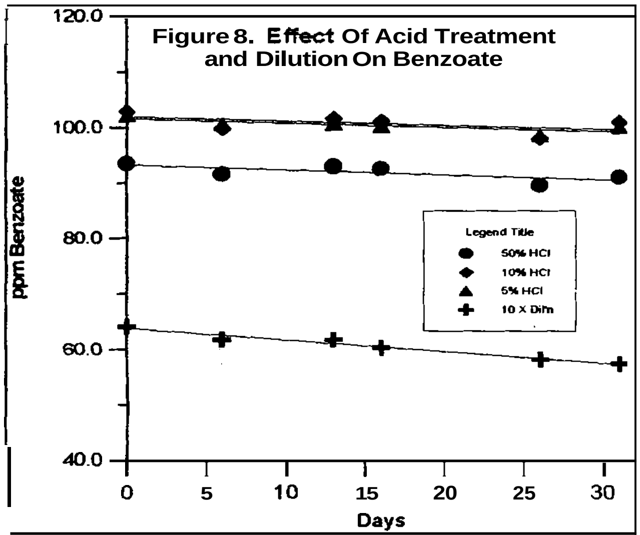

Figure 8. Effect Of Acid Treatment and Dilution On Benzoate

Results show that samples stored in the refrigemtor, treated with azide, and both azide-treated and refrigerated, incur similar of losses of sodium benzoate. Losses after 31 days of storage only range from **1.4** - 2.6%. For the untreated sample, however, *sharp* decline in the concentration was noted with losses of up to 17% after 31 days. These results confirm that microbial action is responsible for the degradation of sodium benzoate. This, however, can be controlled by either cold storage or addition of 0.1% sodium azide. Acid treatment, as shown by the results in Figure 8, also deters this microbial action against sodium benzoate.

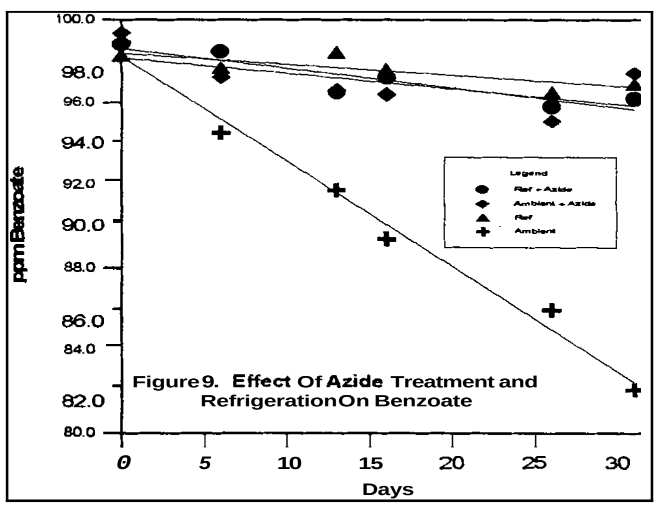

Figure 9. Effect Of Azide Treatment and Refrigeration On Benzoate

The holding time of sodium benzoate was further determined following the procedures set in ASTM (1994). Initial precision study was made by doing multiple analysis of freshly collected, acidified brine samples to establish control limits. The same samples were analyzed at different time intervals up to two weeks. Results are shown in Figure 10. Holding time is only 8 days which is mainly due to the very narrow control band established as a result of the very high precision of the analysis. Similar results were obtained for refrigerated, unacidified samples. Actual decline, however, is only 1.9% which corresponds to a systematic error of the method exceelng the 99% confidence interval.

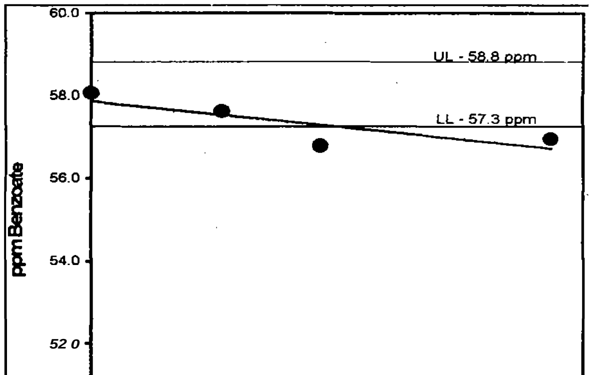

Figure 10. Holding Time For Sodium Benzoate

4.0 CONCLUSIONS

Sodium benzoate in brine matrix can be determined with high precision, accuracy and speed using the Shimadzu HPLC system with the following operating parameters: Methanol-phosphate buffer eluent (55:45, isocratic), flow rate of 1.0 mL/minute for a 150 mm x 4.6 mm id ODS column, at 230 nm wavelength. The method can be relied to give accuracy greater than 99% and COV of less than 1%.

Benzoate is readily degraded due to microbial attack whch can be controlled by either of the following: Acid treatment, refrigeration, or addition of 0.1% sodium azide. Brine matrix does not contribute to a significant interference in benzoate analysis.

Sample treatment with 5-50% HCl retards silica polymerization allowing for easy filtration of the samples through a 0.45 μm filter membrane. Nitric acid is inappropriate to use for sample treatment due to its large absorbance at 230 nm. Sample dilution is also not appropriate as sample treatment as it offers no protection against microbial action.

Holding time for sodium benzoate is eight days for acidified brine samples.

5.0 References

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