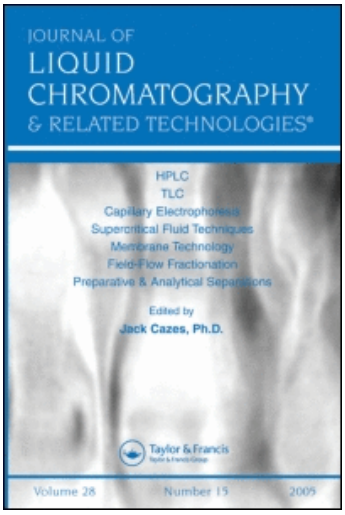

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Determination of Dialkyldimethylammonium Salt in Rolling Oil

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DETERMINATION OF DIALKYLDIMETHYL-AMMONIUM SALT IN ROLLING OIL

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ABSTRACT

DuPont Zorbax™ C8 and Nucleosil™ CN columns were used to quantitatively and qualitatively determine Arquad™ 2C-75 additive[1] in the rolling oils and the residual oils extracted from rolled aluminum products using an Indirect Photometric Chromatography (IPC) method. Two negative peaks were shown in the IPC chromatograms for most of the standard samples. The most important thing is that the first negative peak is believed to be an indication of the presence of quaternary ammonium salts. The results obtained from the analyses of several commercial quaternary ammonium salts, amines and a normal paraffin oil in different solvent systems confirm this observation. These standard compounds include dioctadecyldimethylammonium bromide, octadecyltrimethylammonium bromide, cocoamine and dimethylcocoamine. However, the chromatographic condition can only separate quaternary ammonium salts (negative peak #1) from hydrocarbons and amines (negative peak #2). That means the chromatographic condition is unable to distinguish the differences between quaternary ammonium salts or the differences between amines and a normal paraffin oil. Less than 25 ppm of Arquad 2C-75 additive were detected in the used rolling oil samples and the residual oil samples extracted from the suspect foils. The concentrations

[1] Term Arquad will be used to identify additive distributed by Armak Company.

of Arquad 2C-75 additive determined in the oil samples by the HPLC method are lower than those obtained by a colorimetric method.

INTRODUCTION

At times, molecular or ion determinations by liquid chromatography (HPLC) are often frustrated not only by separation problems but also by detection problems. An example is the problem of detecting ions or compounds that are not UV absorbing. The refractive index detector (RID) can be used, but it is less sensitive than the UV detector. In 1982, Small and Miller (1) developed an HPLC method named Indirect Photometric Chromatography (IPC) from the concept that photometers may be used to detect these "transparent" species. Since then, the theories and applications of the IPC method have been discussed in several publications (2-5). In general, the IPC method involves measuring the absorbance decrease as the analyte displaces a UV active component (e.g. phthalate or toluenesulfonic acid) of the mobile phase. As the UV transparent analyte travels through the LC column, it displaces an equivalent concentration of the UV active eluent ion in the mobile phase. Therefore, the UV detector responds to the presence of the analyte by producing a "negative" peak in the baseline. The negative peaks represent the UV-transparent species determined by the IPC method.

The magnitude of the negative peak is directly related to the differences in concentration and the molar absorptivity between the eluent and analyte species. The positive deflection is due to the ion exchange displacement of p-toluenesulfonic acid (eluent) by the injected sample as a whole on the column (2-4). Since the total equivalent concentration of the sample exceeds that of the eluent, the disturbance is positive.

Quaternary ammonium salts, known as cation surfactants, can be analyzed by using colorimetric (6), TLC (7), GC/MS (8), MS/MS (9), ion chromatography (IC), and HPLC methods (5, 10, 11). In industry, dimethyldicocoammonium chloride is used as an anti-static agent in a certain phase of the aluminum process. It is not used in the rolling oil of final pass reductions on aluminum products. This method allows for monitoring against accidental additives or contamination of the rolling oils. Therefore, the concentrations of Arquad 2C-75 additive in the rolling oil and in the residual oil on aluminum products is of interest. An HPLC method was developed to determine trace amounts of Arquad 2C-75 additive in the rolling oil components. The composition of Arquad 2C-75 additive, as reported by the manufacturer, is as follows: 75% of active quaternary ammonium salt ($R_2(CH_3)_2N^+Cl^-$), 1% of free amine and ammonium chloride and 24% of aqueous-isopropanol. In fact, a mixture of dialkyldimethylammonium salts is present in Arquad 2C-75 additive. The hydrocarbon length distribution for the alkyl group (R) in Arquad 2C-75 additive is listed below:

R =	octyl	5%
	decyl	6%
	dodecyl	51%
	tetradecyl	19%
	hexadecyl	9%
	octadecyl	5%
	octadecenyl and/or octadecadienyl	5%

Since the quaternary ammonium cations cannot absorb UV light, the IPC method was introduced to quantitatively and qualitatively determine Arquad 2C-75 additive in the rolling oils and residual oils extracted from aluminum samples using Dupont Zorbax™ C8 and Nucleosil™ CN columns.

EXPERIMENTAL

1. Apparatus:
   Spectra-Physics 8100 liquid chromatograph
   Spectra-Physics 4200 computing integrator
   Spectra-Physics 8440 variable wavelength UV/VIS detector
2. Chromatographic Conditions:
   UV wavelength: 260 nm
   AUFS: 0.32
   Attenuation (AT): 2
   Peak Width (PW): 6
   Peak Threshold (PT): 120
3. Column:
   DuPont Zorbax^{TM} C8 reverse phase column (4.6 x 250 mm)
   Alltech Nucleosil^{TM} CN column (5 m, 4.6 x 150 mm)
4. Mobile Phase:
   25% methanol / 75% water with 5 mM p-toluenesulfonic acid.
5. Reagents:
   Arquad 2C-75 additive (Armak Co.)
   dioctadecyldimethylammonium bromide (Kodak)
   octadecyltrimethylammonium bromide (Fluka AG.)
   dimethylcocoamine (Wisco)
   cocoamine (Wisco)
   p-toluenesulfonic acid (Fisher)
   water (HPLC, B&J)
   methanol (HPLC grade, B&J)
   isooctane (HPLC grade, B&J)
   hexane (HPLC grade, B&J)
   methylene chloride (HPLC grade, B&J)
6. Sample Preparation:
   (a) Isooctane (400 ml) and a Soxhlet extractor were used to extract the residual oils from 30 ft^2 aluminum samples for one hour. The extracts were concentrated to 200 microliters and then subjected to the IPC method.

(b) The rolling oil samples and normal paraffin oil were directly analyzed by the HPLC method without any dilution.

(c) The dioctadecyldimethylammoniun bromide, octadecyltrimethylammonium bromide, dimethylcocoamine and cocoamine were prepared by dissolving them in the mobil phase solution or in hexane, isooctane, acetone, or methylene chloride for the preparations of 10-1000 ppm solutions.

(d) The decomposition products of Arquad 2C-75 additive were prepared by heating the neat Arquad 2C-75 additive at 200°C in a glass beaker for 1, 2, 4, & 7 hours. Then the decomposition products were dissolved in isooctane for the preparation of a 1000 ppm solution.

(e) All of the HPLC samples were filtered using a Millipore HV 0.45 micron filter before injection. A Spectra Physics SP8100 autosampler equipped with a 10 l loop was used in these studies.

RESULTS AND DISCUSSION

A. Method Development

The use of HPLC in the determination of trialkylmethylammonium salts has been reported (5). Helboe used a Nucleosil™ CN column with the IPC method to separate several triakylmethylammonium salts. We modified this analytical technique to determine dialkyldimethylammonium salts (Arquad 2C-75 additive) in the rolling oils. A DuPont Zorbax™ C8 column was also used for this study. Figure 1 indicates that three negative peaks and a positive deflection are shown in the LC chromatograms of 100 and 1000 ppm

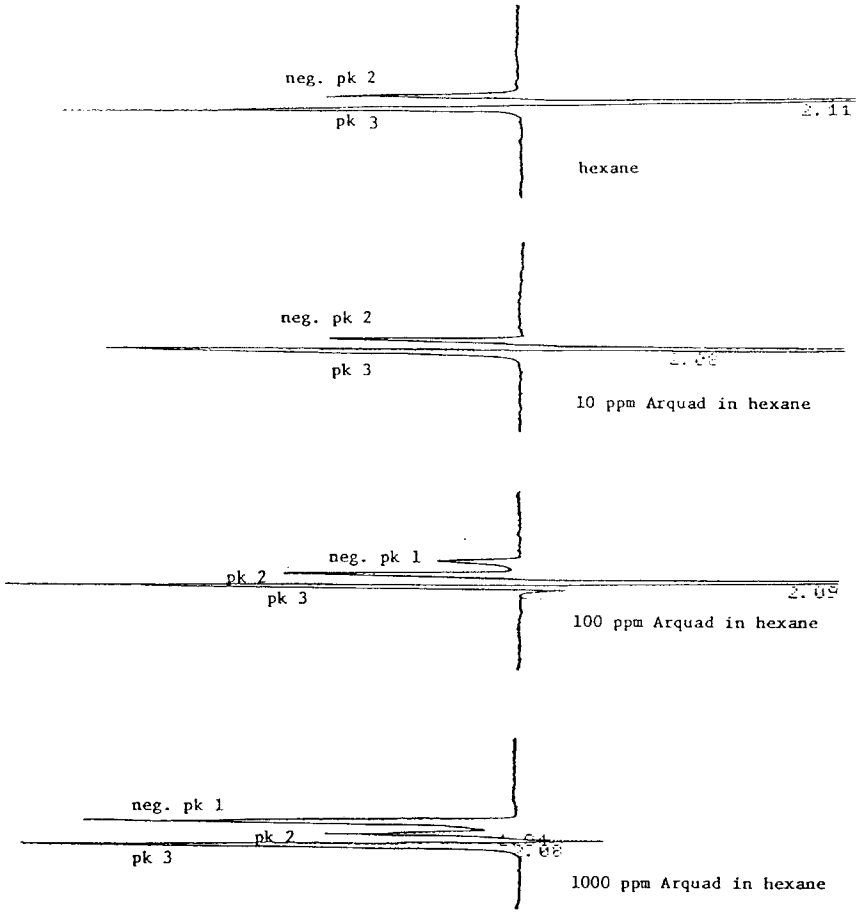

FIGURE 1. Chromatograms of Arquad 2C-75 in Hexane (Nucleosil CN column, AT=2)

Arquad 2C-75 additive in hexane, while only two negative peaks and a positive deflection are shown in the chromatograms of a 10 ppm Arquad 2C-75 additive sample and a pure hexane sample.

Similar LC chromatograms were obtained with the use of a Zorbax™ C8 column (Figure 2). Two negative peaks instead of three negative peaks were detected in the LC chromatogram of a 750 ppm Arquad 2C-75 additive

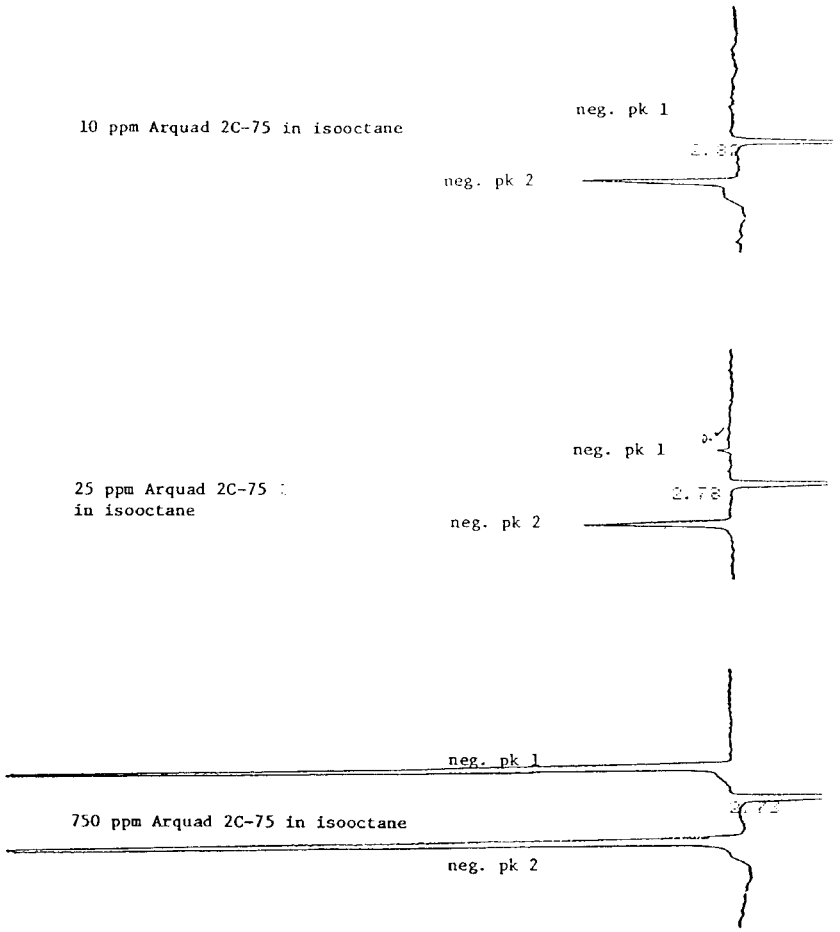

FIGURE 2. Chromatograms of Arquad 2C-75 in Isooctane (Zorbax C8 column, AT=2)

sample using the Zorbax™ C8 column. Referring to the chromatograms of hexane (Figure 1) and isooctane (Figure 2), which are the solvents used to dissolve the analytes, the first negative peak is believed to be an indication of the presence of Arquad 2C-75 additive in the solutions. Negative peak #1 is associated with the Arquad 2C-75 additive as evidenced by the fact that its peak height is proportional to the concentration of Arquad 2C-75 additive injected as the results show in Figures 7 and 8. Two linear calibration curves (peak height vs ppm of Arquad 2C-75 additive) were obtained. The third negative peak represents the components of isooctane, hexane, amines or other unknown compounds in the samples. It is believed that the presence of the second negative peak in Figure 1 is due to the refractive index change of the mobile phase. According to the LC results (Figures 1 and 2), the detection of Arquad 2C-75 additive by using the Zorbax™ C8 column is twice as sensitive as when using the Nucleosil™ CN column. The minimum detectable concentration of Arquad 2C-75 additive in isooctane is 25 ppm using a Zorbax™ C8 column.

Dioctadecyldimethylammonium bromide (DOMB), octadecyltrimethylammonium bromide (OTMB), dimethylcocoamine (DMCA), cocoamine, and normal paraffin oil were analyzed as references under the same chromatographic conditions. The LC chromatograms of dimethylcocoamine, cocoamine, and the mixture of these two amines were obtained by the IPC method. The chromatograms in Figure 3 indicate that the presence of negative peak #2 is due to these two amines, but the chromatographic conditions are not suitable for the separation of the amines. Normal paraffin oil is also detected at the same retention time (Figure 9) as the amines. As the results show in Figure 4, the chromatograms of Arquad 2C-75 additive, dioctadecyldimethyl and octadecyltrimethylammonium

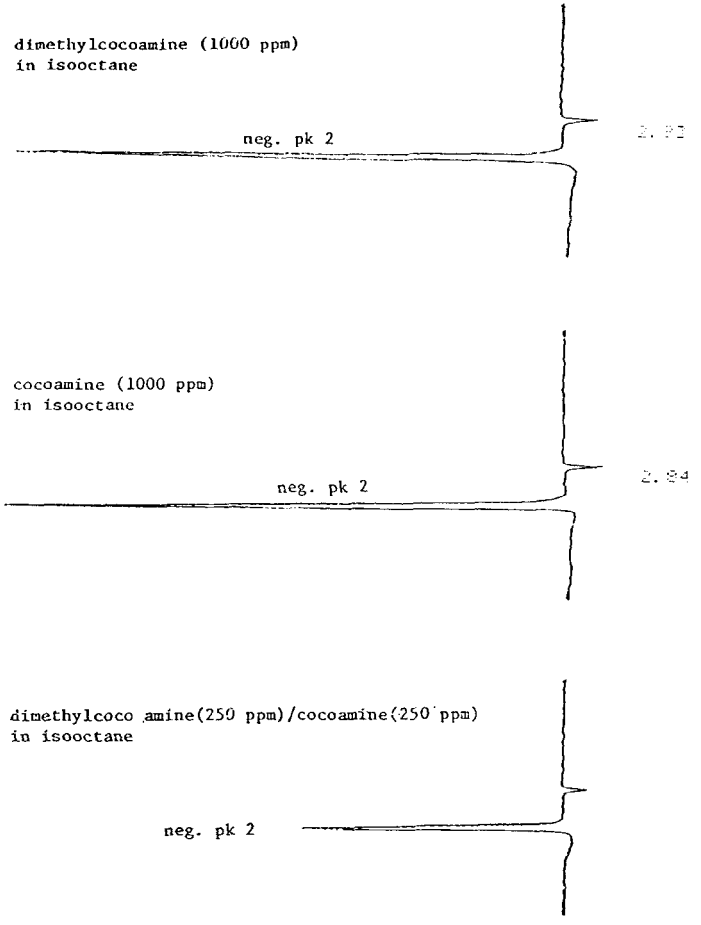

FIGURE 3. Chromatograms of Alkylamines in Isooctane (Zorbax C8 column, AT=4)

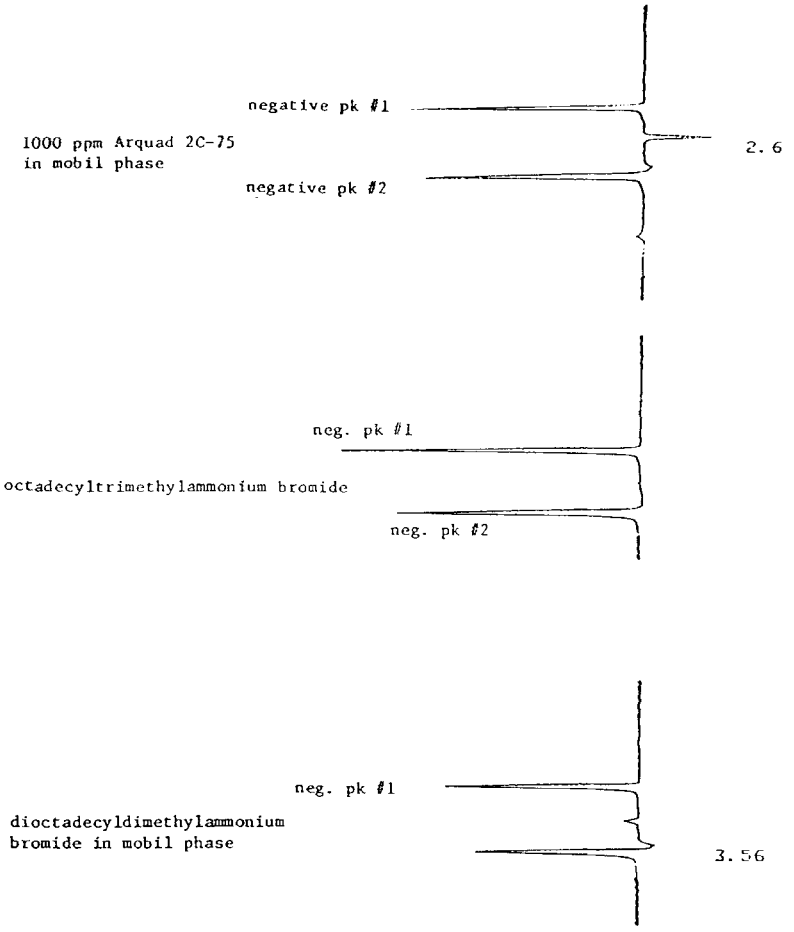

FIGURE 4. Chromatograms of Arquad 2C-75 and Quaternary Ammonium Bromides in Mobil Phase (Zorbax C8 column, AT=4)

bromides dissolved in the mobile phase (25% MeOH in water with 5 mM p-toluenesulfonic acid) are very comparable. Two negative peaks were present in the HPLC chromatograms. Different solvent systems which were used to dissolve the quaternary ammonium salts were evaluated to ensure that the first negative peak in the LC chromatograms of Arquad 2C-75 additive, DOMB, and OTMB samples represents the elution of the quaternary ammonium salt. Acetone and methylene chloride were used in these studies. The chromatograms of methylene chloride, DOMB, OTMB, and Arquad 2C-75 additive samples in methylene chloride are provided in Figure 5. Two negative peaks are shown in the chromatograms except for the DOMB samples. The chromatograms in Figure 6 show that only one negative peak (#1) was detected when using acetone as a dissolving solvent.

Summarizing all of these HPLC results obtained from the Arquad 2C-75 additive, DOMB, OTMB, DMCA, cocoamine, and normal paraffin oil prepared in the different solvent systems, we believe that peak #2 in the IPC chromatograms is the detection of amines and hydrocarbons, and the first peak in the LC chromatogram of the Arquad 2C-75 additive sample must indicate detection of quaternary amines.

B. Analyses of Oil and Aluminum Samples

Two calibration curves (Figures 7 and 8) were established to quantitatively determine Arquad 2C-75 additive in the rolling oils or in the residual oils extracted from aluminum samples. Meanwhile, two standard Arquad 2C-75 additive solutions in normal paraffin oil were analyzed by HPLC to ensure that ppm levels of Arquad 2C-75 additive can be detected in the oil samples. According to the LC results of these oil samples (tank #7, 8, 9, and 10) (Figure 9) and the data

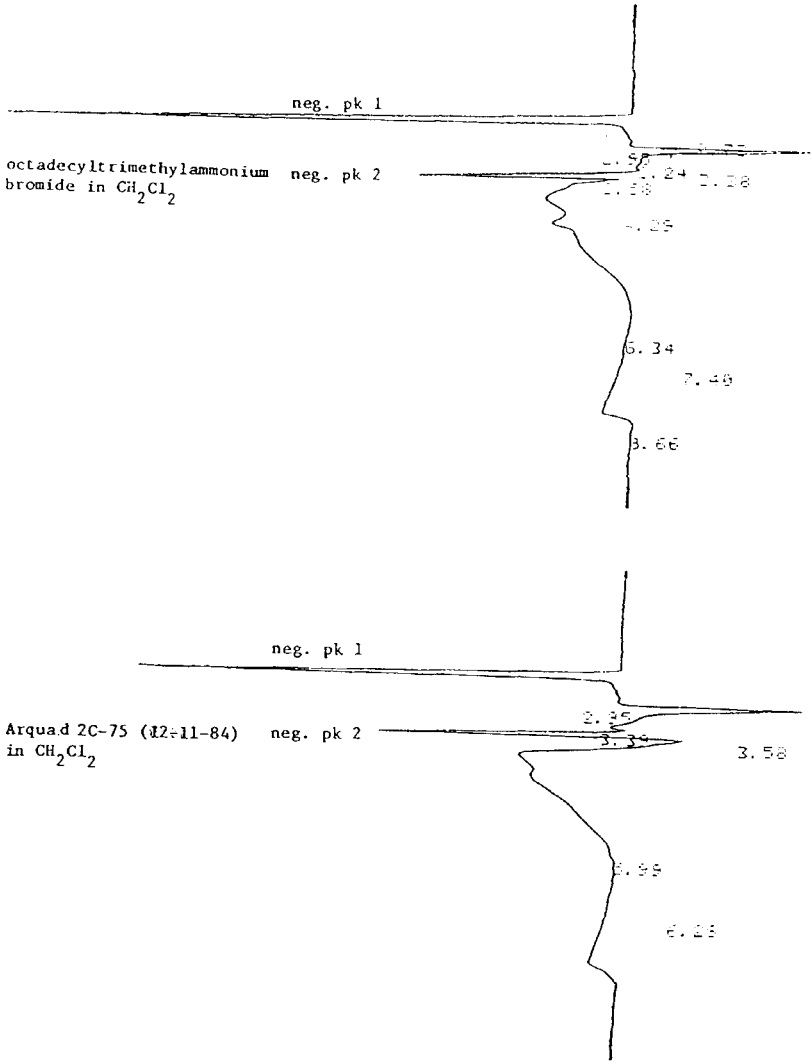

FIGURE 5. Chromatograms of Arquad 2C-75 and Quaternary Ammonium Bromides in Methylene Chloride (Zorbax C8 column, AT=4) (con't) Continued...

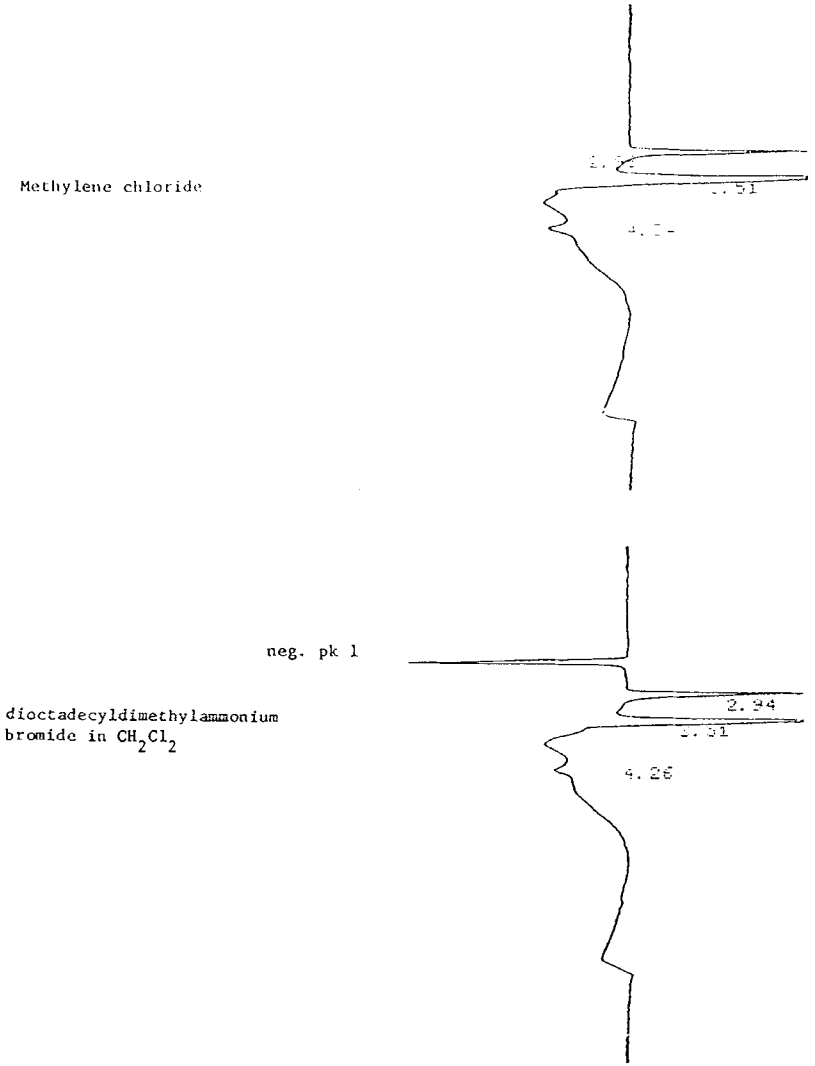

FIGURE 5. Chromatograms of Arquad 2C-75 and Quaternary Ammonium Bromides in Methylene Chloride (Zorbax C8 column, AT=4) Continued...

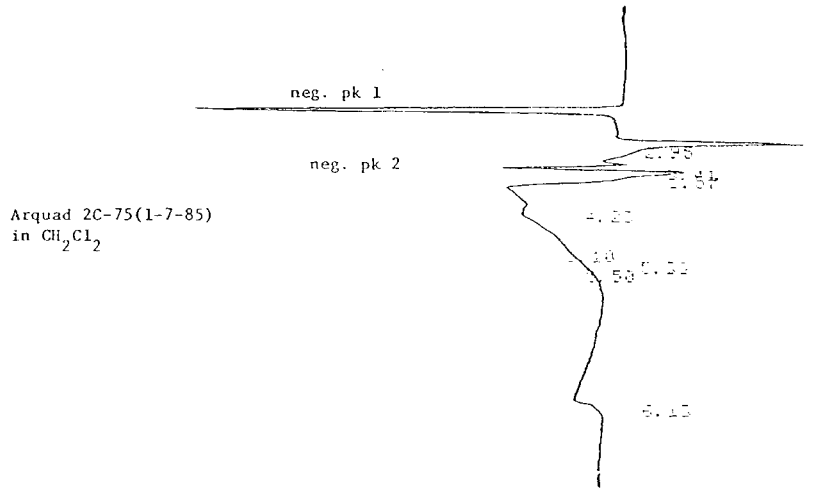

FIGURE 5. Chromatograms of Arquad 2C-75 and Quaternary Ammonium (con't) Bromides in Methylene Chloride (Zorbax C8 column, AT=4)

of aluminum samples (A, B, and C) (Figure 10), less than 25 ppm of Arquad 2C-75 additive are present in these oil samples. However, these results are very different from those obtained by the colorimetric method (6) (Table 1). In the colorimetric analyses, the reagent can react with quaternary amines to form a yellow color complex which absorbs UV light at 425 nm. Therefore, any yellow color impurities in the rolling oils can affect these analytical results. This may be one of the reasons that the levels of Arquad 2C-75 additive determined by the colorimetric method are higher than those obtained from the IPC methods.

The decomposition rate of Arquad 2C-75 additive at 200°C was also investigated. The decomposition product of Arquad 2C-75 additive was prepared as the procedure shows in the experimental section and analyzed by the HPLC method as well as fresh Arquad 2C-75 additive. As

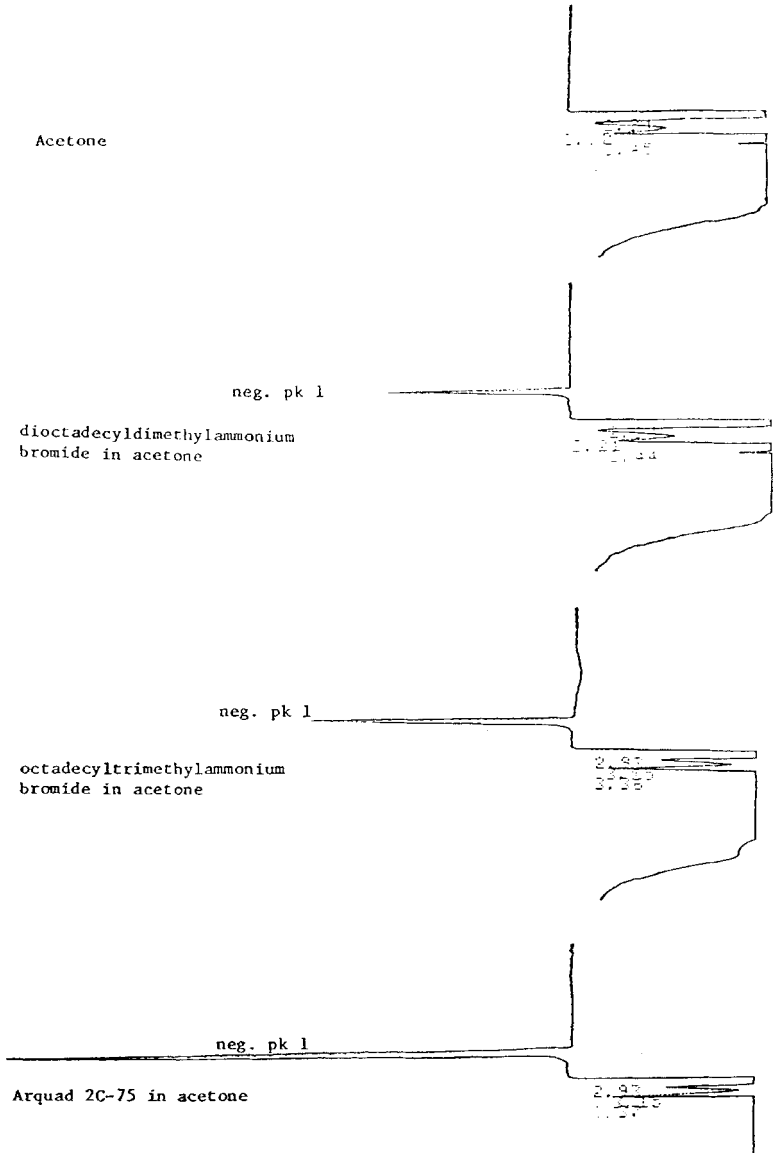

FIGURE 6. Chromatograms of Arquad 2C-75 and Quaternary Ammonium Bromides in Acetone (Zorbax C8 column AT=4)

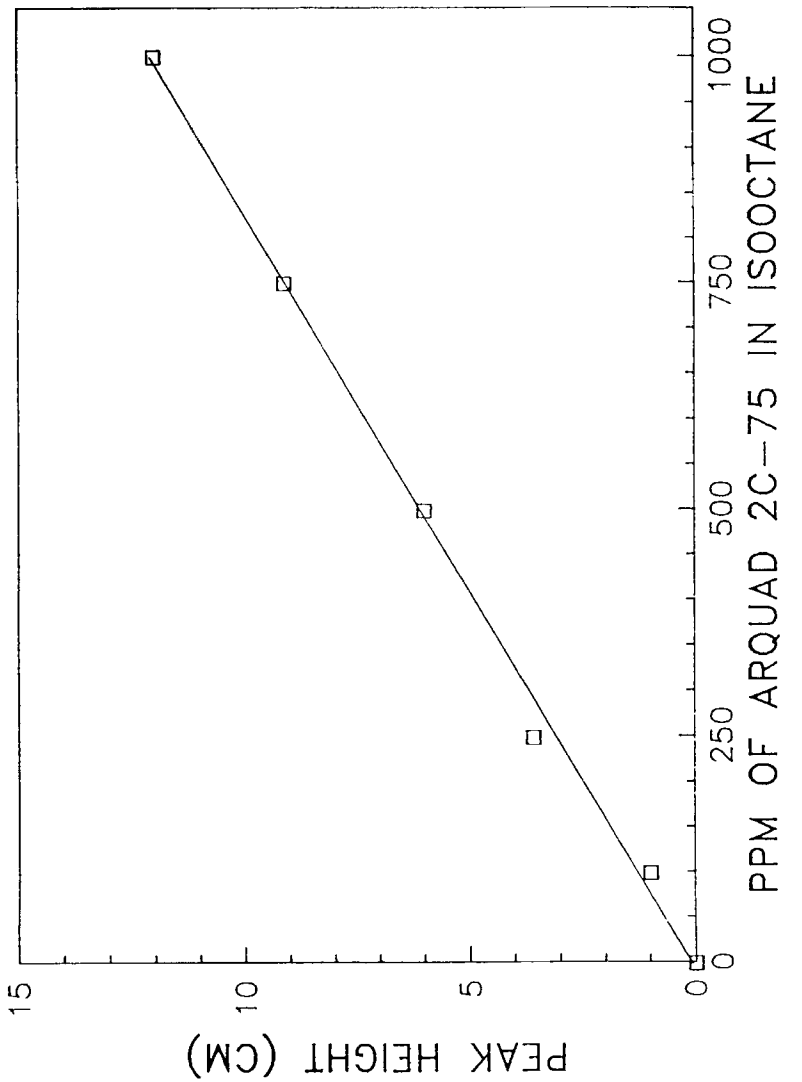

FIGURE 7. Calibration Curve for Nucleosil CN Column

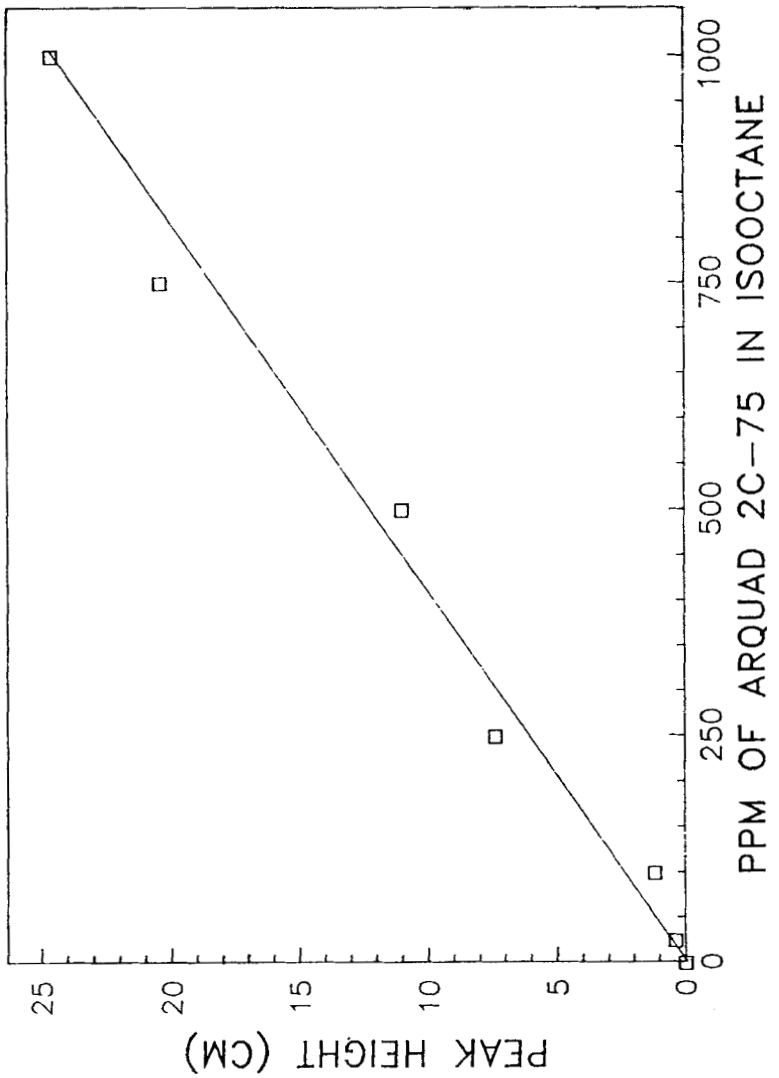

FIGURE 8. Calibration Curve for Zorbax C8 Column

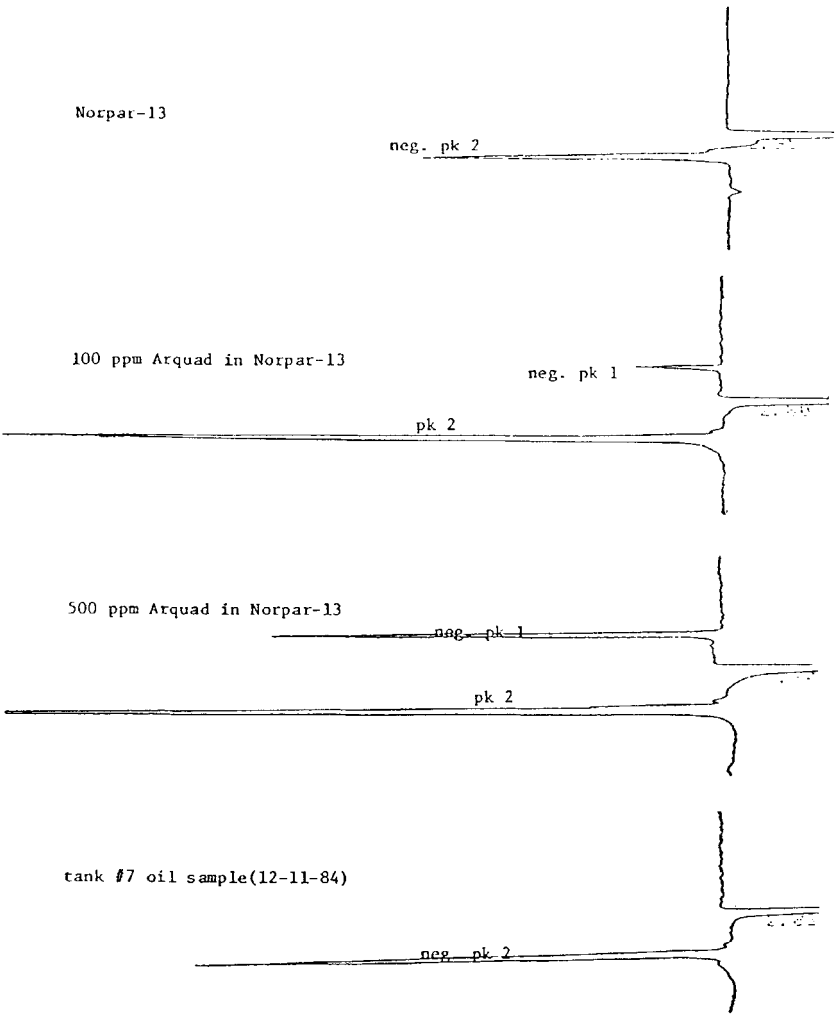

FIGURE 9. Chromatograms of a Normal Paraffin Oil, Arquad in a Normal Paraffin Oil, and Used Rolling Oils (Zorbax C8 column AT=2)

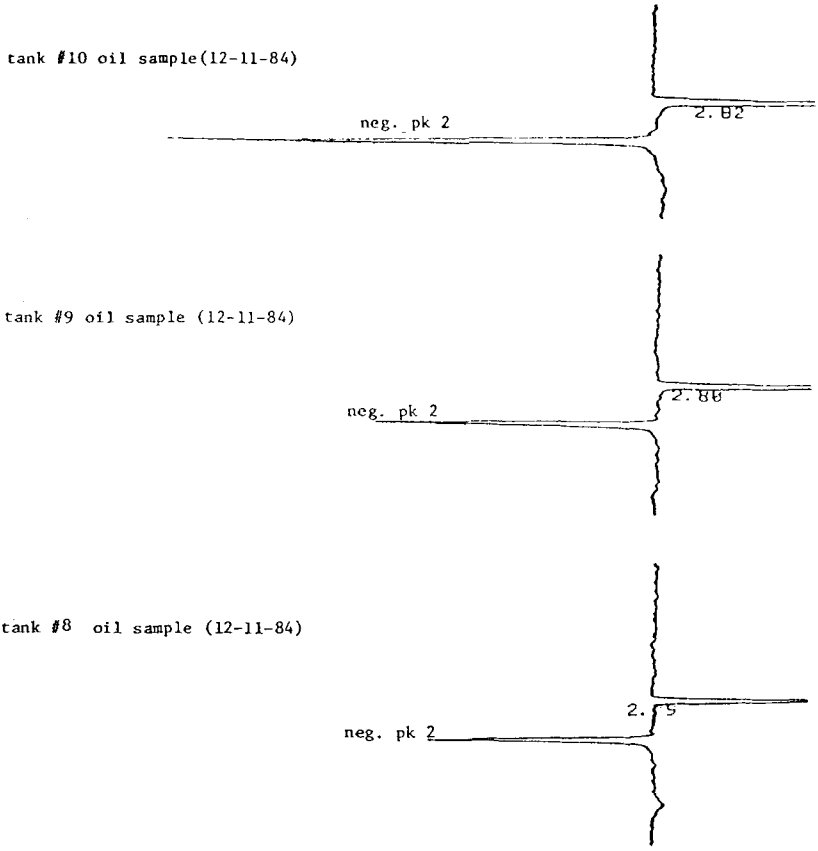

FIGURE 10. Chromatograms of Residual Oils Extracted from Aluminum Samples (Zorbax C8 column AT=2)

Continued...

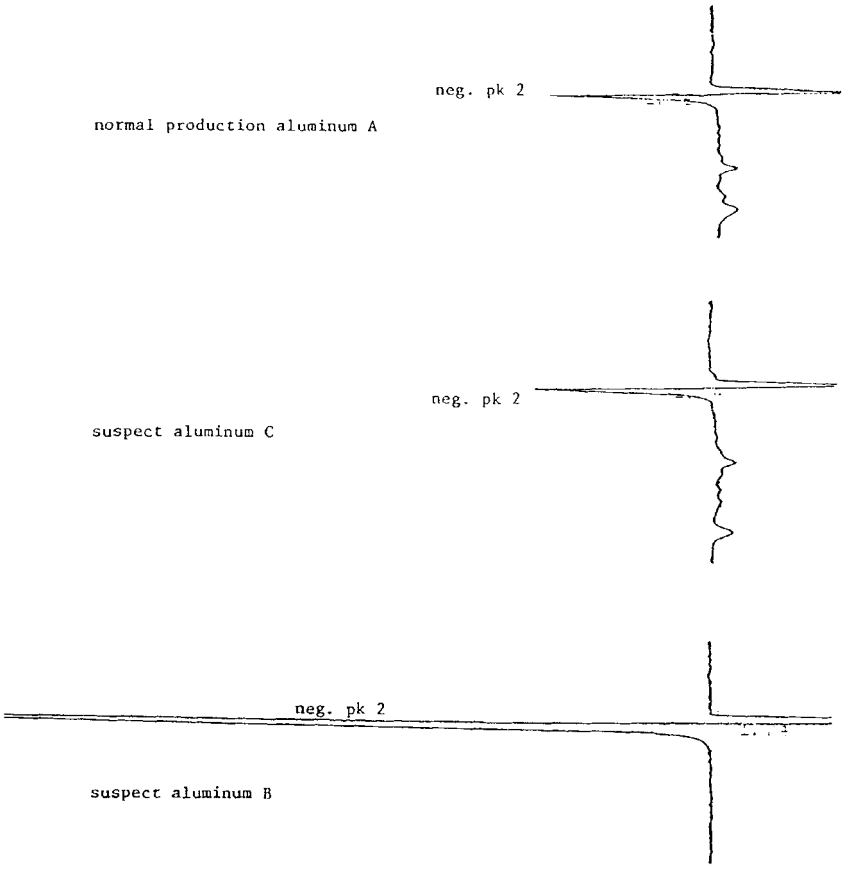

FIGURE 10. (con't) Chromatograms of Residual Oils Extracted from Aluminum Samples (Zorbax C8 column AT=2)

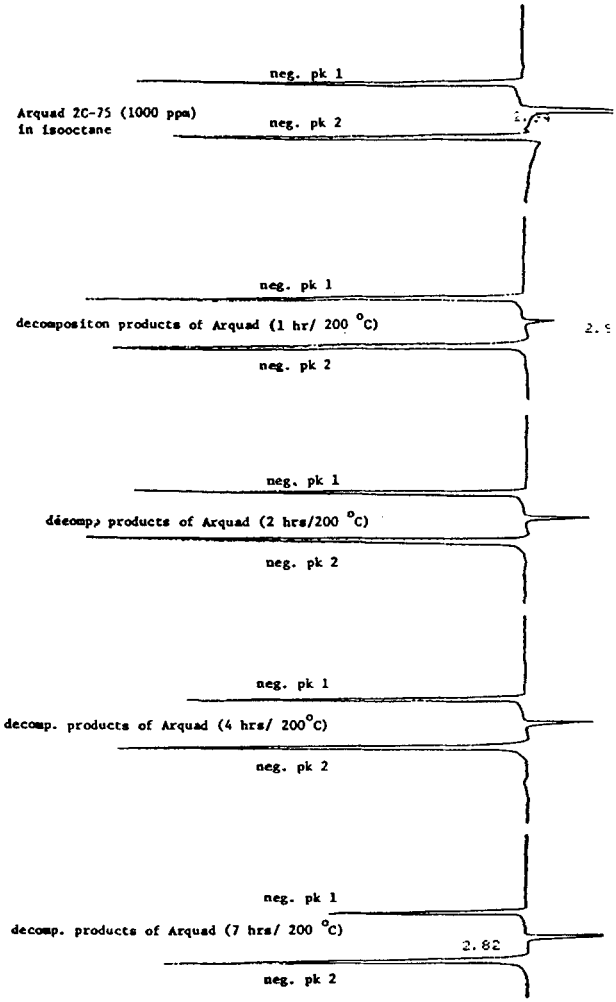

FIGURE 11. Chromatograms of Decomposition Products of Arquad 2C-75 in Isooctane (Zorbax C8 column AT=4)

TABLE 1

Amounts of Arquad 2C-75 Additive Determined by HPLC and Colorimetric Methods

Sample I.D	Amounts of Arquad (HPLC)	Amounts of Arquad (Colorimetric)
Tank #7 Oil	<25 ppm	278 ppm
Tank #8 Oil	<25 ppm	254 ppm
Tank #9 Oil	<25 ppm	149 ppm
Tank #10 Oil	<25 ppm	176 ppm
Aluminum A	<25 ppm	0 micrograms
Aluminum B	<25 ppm	35 micrograms
Aluminum C	<25 ppm	0 micrograms

the LC results show in Figure 11, about 50% of Arquad 2C-75 additive is decomposed after 7 hours at 200°C. This decomposition rate is not as rapid as that reported in the literature (6).

CONCLUSION

Overall, the IPC method is a sensitive and reproducible method for the determination of Arquad 2C-75 additive in the rolling oils and residual oil samples. Although individual quaternary ammonium salts can not be separated by this method, the method does allow the quantitative and qualitative determination of Arquad 2C-75 additive in the rolling oils and the residual oils extracted from aluminum samples.

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