Determination of Gafac in complex solution matrices

by S. A. Schubert

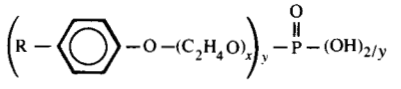
A new analytic method is described for determining the concentration of Gafac Re-610 (trademark of the GAF Corporation, New York, NY) in multicomponent solutions. This method utilizes a simple methylene chloride extraction to separate the Gafac from interfering chemical species, such as cupric sulfate. The ultraviolet absorbance of the methylene chloride extract is then measured at 276 nm and is shown to be proportional to the concentration of Gafac over the range of 1–170 ppm. However, this relationship is nonlinear except for concentrations less than 15 ppm. The limit of detection is 0.6 ppm and the relative precision at the 10-ppm level is ±6%. Experiments to optimize and characterize various aspects of the analytical procedure are described, including determining the absorptivity of Gafac, measuring the distribution ratio, calculating extraction efficiencies, optimizing the extraction pH, and evaluating selected spectral interferences.

Introduction

Surface-active agents have applications in a variety of industrial products and processes. Surfactants fall into three basic categories: detergents, wetting agents, and emulsifiers. Although such compounds typically are present in low concentrations, they can significantly influence the behavior of a process or a product.

The analysis of surfactants depends considerably on the matrix involved. In the simplest situations, physical properties such as surface tension [1, 2] or polarographic adsorption [3, 4] may be used to quantitate the level of surfactant present in a solution. Unfortunately, such test methods are by nature relatively nonspecific and can be influenced greatly by variables other than surfactant concentration. Solution temperature, ionic strength, and specific gravity are among the factors that are often difficult to control. Chemical methods of analysis are not without interferences, but they manage to avoid many of the problems of physical methods by monitoring characteristic functional groups such as phosphates [5], sulfates [6, 7], or amines [8–10]. These methods usually depend on a prior separation, digestion, or complexation step to isolate the species of interest.

Plating solutions represent perhaps one of the most challenging matrices for the determination of surfactants because the chemical and physical interferences abound. Gafac Re-610 is typical of the surface-active agents employed in many copper plating baths. Although Gafac is a proprietary compound, it is known that it is an organic phosphate ester with the following empirical structure [11]:



The analytical method described in this paper exploits the presence of the aromatic functionality to determine the concentration of Gafac. The proposed analytical method consists of two parts:

1. Separation of Gafac from interfering chemical species by solvent extraction.
2. Analysis of the extracted Gafac by ultraviolet spectrophotometry.

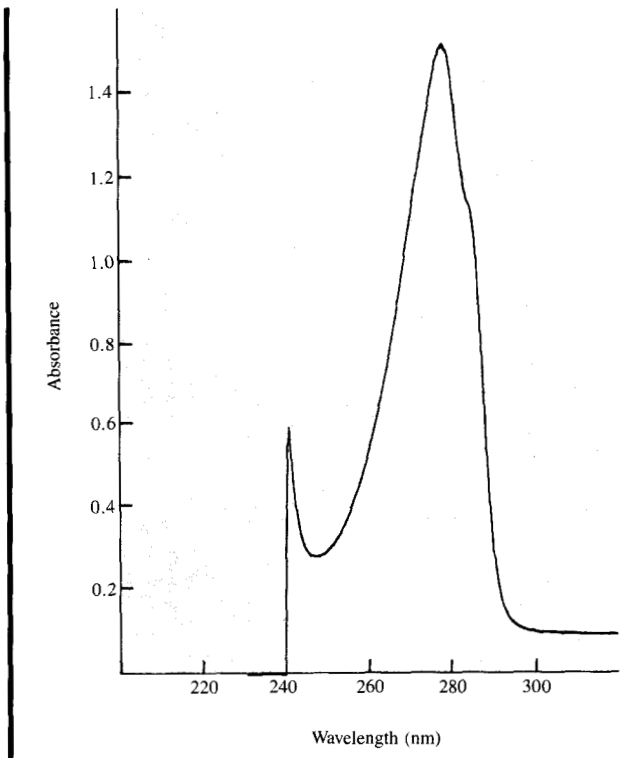


Figure 1

Typical ultraviolet absorbance spectrum of aqueous Gafac Re-610.

This paper describes the optimization and characterization of the above analytical method for determining Gafac in complex aqueous solutions such as copper plating baths.

Experimental procedures

• *Spectra*

Ultraviolet absorbance was measured with a Beckman Model 26 spectrophotometer. The region from 320-240 nm was scanned at a rate of 20 nm/min and the resulting absorbance spectra recorded with a wavelength resolution of 20 nm/in. Sample and reference cells were 1-cm quartz cuvettes. The reference cell was fitted with a stopper of Teflon (trademark of E. I. du Pont de Nemours & Co., Inc., Wilmington, DE) to minimize evaporation of the solvent.

• *Extraction efficiency*

A 49-ppm Gafac standard in DI water was used to determine the extraction efficiency of methylene chloride. An aliquot of the Gafac standard was adjusted to pH 4, then extracted once with an equal volume of methylene chloride. The ultraviolet absorbance of the aqueous fraction was measured before and after extraction. The experiment was repeated using two more aliquots of the same Gafac standard.

• *Optimization of pH*

The pH of samples prior to solvent extraction was optimized by taking several aliquots of the same plating bath solution, adjusting each aliquot to a different pH, then extracting and comparing the resulting absorbances. Five different pH values were tested: 7.0, 6.0, 5.0, 4.0, and 3.0.

• *Interferences*

Potential spectral interferences of the type that might occur in a copper plating bath were screened by obtaining ultraviolet spectra of aqueous solutions containing 0.04 M cupric sulfate, 0.02 M EDTA, or 0.29 M sodium formate. For comparison, a pH 4 mixture of cupric sulfate (0.04 M) and EDTA (0.14 M) was extracted with an equal volume of methylene chloride and the absorbance spectrum of the extract was obtained.

• *Standards*

Surfactant standards were prepared by dissolving known amounts of Gafac Re-610 in deionized water. Potentially interfering matrices were synthesized by making standards 0.14 M in EDTA and 0.04 M in cupric sulfate, which also served to maintain a constant ionic strength. Appropriate pH adjustments were made with dilute (25% v/v) sulfuric acid. All samples were extracted with glass-distilled methylene chloride. Extractions were carried out at room temperature, 22 ± 2°C. Calibration curves were generated over the concentration range of 0.5–210 ppm.

Results and discussion

• *Absorbance spectrum*

Gafac has an ultraviolet absorbance spectrum with a pronounced absorbance maximum centered at 276 nm, as shown in **Figure 1.** This absorption behavior is characteristic of a benzenoid compound and corresponds to the so-called "B-band" absorption associated with π-π^* electronic transitions. Compared to unsubstituted benzene, which has a weak absorbance at 255 nm [12], Gafac exhibits a strong B band that is shifted to longer wavelengths by over 20 nm. This apparent bathochromic shift can be explained by the presence of both an electron-donating ethoxy-ester group and a para-alkyl substituent.

An interesting property of surfactants, the formation of micelles, is detected by looking at the absorptivity of methylene chloride extracts as a function of the initial aqueous Gafac concentration. Based on the assumption that Beer's law holds for dilute Gafac solutions, an absorptivity (E) can be defined, even though the formula weight is unknown, by using the following expression:

$$E = A/bc, \tag{1}$$

where A is the absorbance, b is the path length of the cell in centimeters, and c is the concentration of Gafac in g/100 ml.

Apparent absorptivities were calculated for the different conditions indicated in **Table 1.** At higher concentrations the absorptivity appears to decrease dramatically. Such behavior is not uncommon in other chemical systems and is probably due to the formation of micelles. Surface-active materials such as Gafac are known to aggregate into micelles, where the hydrophilic groups protrude into the solution and the hydrophobic hydrocarbon moieties cluster together in the interior of the micelle. This gives the exterior of the micelle hydrophilic properties which make extraction into an organic solvent less facile.

As the surfactant concentration increases, the propensity for micelle formation increases and the subsequent extraction efficiency decreases. The net result, as evidenced in Table 1, is that the absorptivity appears to be concentration-dependent when, in actuality, the Gafac concentration of the extract is varying because of micelle formation.

Table 1 Absorptivities for Gafac Re-610.

Initial Gafac (ppm)	*Extracted*	*Final expected* Gafac* (ppm)	*E* (1%, 1 cm)
50	No	50	22
1–10	Yes	1–5	33
20–80	Yes	10–40	20
80–170	Yes	50–80	12

* For samples that were extracted, the expected Gafac concentrations were calculated by assuming a constant extraction efficiency of 0.47.

Extraction efficiency

Assuming ideal conditions, the partition of Gafac (G) between two immiscible solvents, water and methylene chloride, can be described by the equilibrium

$$G_w \rightleftarrows G_o, \tag{2}$$

where the subscripts "w" and "o" refer to the respective water and organic phases. The distribution of the total analytical concentration of Gafac in the two phases is given by a distribution ratio D, defined as follows:

$$D = [G_o]/[G_w], \tag{3}$$

where $[G_o]$ is the activity of Gafac in the methylene chloride and $[G_w]$ is the activity of Gafac in the aqueous phase. In this work, the ionic strength was assumed to be relatively constant, as it would be in a plating bath, and molar concentrations were substituted for activities. The concentration of Gafac in the organic phase, $[G_o]$, was determined indirectly by measuring the absorbance of the aqueous phase before and after extraction, $[G_w]_i$ and $[G_w]_f$, respectively. Equation (3) thus becomes

$$D = \frac{[G_w]_i - [G_w]_f}{[G_w]_f} \tag{4}$$

and simplifies to

$$D = \frac{[G_w]_i}{[G_w]_f} - 1. \tag{5}$$

Applying Eq. (5) to the experimental data yields the results listed in **Table 2.** Based on these data, the best value is $D = 0.89 \pm 0.01$. Keeping in mind the results in the previous section regarding micelle formation, this distribution ratio is probably only valid within a narrow range of initial Gafac concentrations. It is still useful, however, for finding the optimum extraction conditions. Optimization of the extraction was pursued within the following constraints:

Table 2 Experimentally determined distribution ratios. (Gafac concentrations are expressed in arbitrary absorbance units.)

Trial	$[G_w]_i$	$[G_w]_f$	D
1	112	60	0.87
2	111	57	0.95
3	112	61	0.84

Table 3 Calculated extraction efficiencies.

Combination	V_o	n	α_o
1	$2\,V_w$	1	0.64
2	$2\,V_w$	2	0.87
3	$1\,V_w$	1	0.47
4	$1\,V_w$	2	0.72

1. Maximize the fraction of Gafac transferred to the organic phase (α_o) to enhance sensitivity.
2. Limit the number of extractions (n) to one or two to simplify the procedure.
3. Minimize the volume of MC (methylene chloride) used (V_o) to avoid disposal problems and to maximize the concentration of Gafac.

All of the above factors are incorporated in the following expression for the extraction efficiency:

$$\alpha_o = 1 - \left(\frac{V_w}{V_w + DV_o}\right)^n. \tag{6}$$

If we let V_o equal some fraction of V_w, choose $n = 1$ or 2, and use $D = 0.89$, the information shown in **Table 3** can be generated using Eq. (6). Combination 3 in Table 3 ($V_o = V_w$ and $n = 1$) satisfies the previously stated criteria for maximum extraction efficiency, with the minimum volume of solvent and the smallest number of extractions.

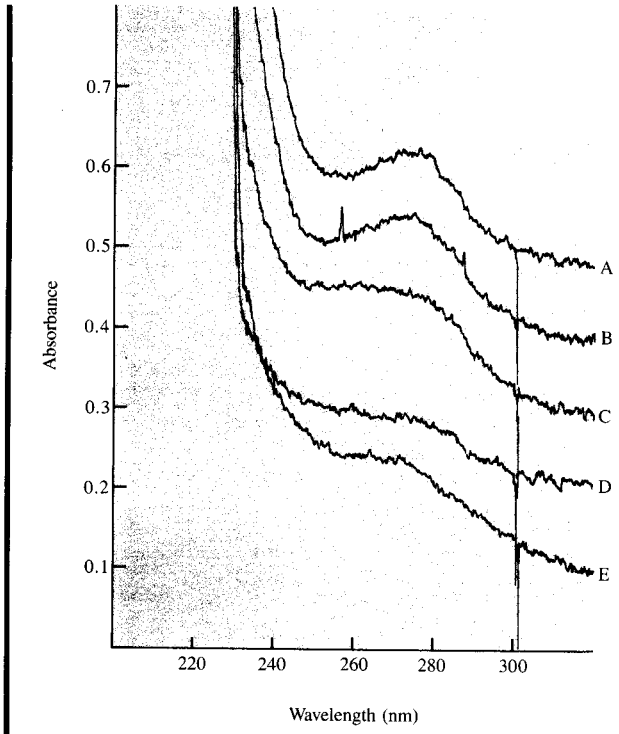


Figure 2

Methylene chloride absorbance spectra obtained by extracting a Gafac-containing plating solution at five different pH's: A = pH 3, B = pH 4, C = pH 5, D = pH 6, and E = pH 7.

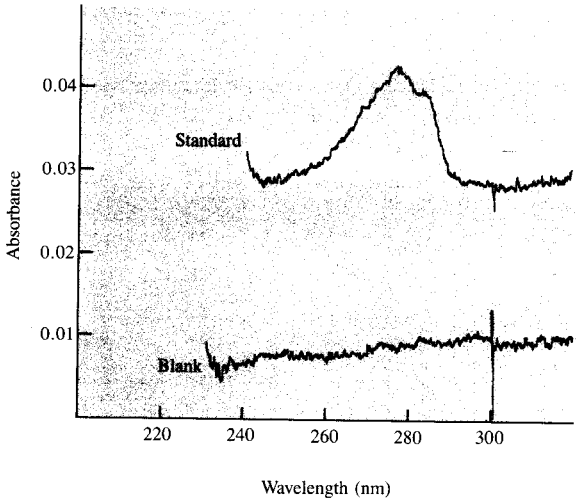


Figure 4

Comparison of methylene chloride absorbance spectra obtained by extracting synthetic plating solution samples containing 5 ppm Gafac (standard) and without Gafac (blank).

• *Optimization of pH*

The extraction of Gafac from a polar solvent (water) into a nonpolar solvent (methylene chloride) is highly pH-dependent. Protonation of the terminal phosphate group reduces Gafac's hydrophilicity, thereby enhancing its extractability.

Because of its uncertain composition and unknown acid dissociation constants, it is not possible to calculate the optimum pH of extraction. This was determined empirically by experimentation. Before these experiments were conducted, the range of most likely pH values was estimated by assuming that Gafac is an analog of phosphoric acid. The first two dissociation constants of phosphoric acid (pK_1 = 2.12 and pK_2 = 7.2) indicate that the pH must be less than 7 in order to even partially protonate Gafac and should be substantially less than 2 to ensure complete protonation. A practical lower limit of pH 3 is dictated, however, if there is the possibility that EDTA is present, since it precipitates from solutions at approximately pH 2.5 or less.

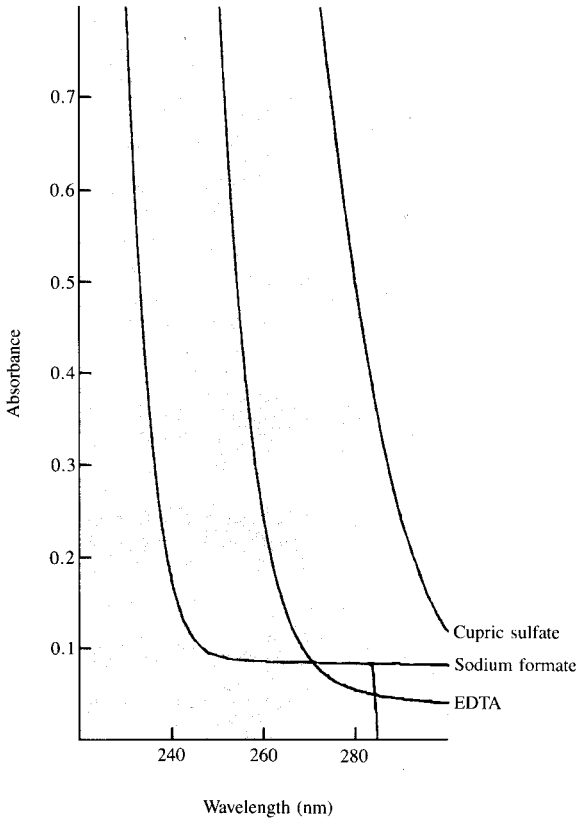


Figure 3

Ultraviolet absorbance spectra of potential chemical interferences: EDTA (0.02 M), sodium formate (0.29 M), and cupric sulfate (0.04 M).

The range of pH 3–7 was tested and the various spectra are shown in **Figure 2.** Clearly, as predicted, a low pH is desirable. Since the responses at pH 3 and pH 4 are similar, pH 4 was chosen as the preferred pH for the extraction to minimize the risk of precipitating species such as EDTA.

• *Interferences*

After it was determined that Gafac had a strong ultraviolet absorption maximum at 276 nm, unsuccessful attempts were made to determine Gafac directly in solutions containing cupric sulfate and EDTA. The ultraviolet absorption of aqueous copper(II) is characterized by an intense charge-transfer band that covers most of the region below 300 nm **(Figure 3).** This problem is compounded by the presence of EDTA, which not only enhances the copper charge-transfer band but contributes its own interfering absorbance below 280 nm (also shown in Fig. 3). Formaldehyde, which is a constituent of many plating baths, is known to absorb only very weakly at 270 nm and was therefore not considered a potential interference [13]. Its degradation product, formate, was tested and found to also be innocuous, as indicated in Fig. 3.

Appropriate pH-adjustment, followed by extraction with methylene chloride, proved sufficient for separating Gafac from interfering species. **Figure 4** compares the absorbance spectra of two methylene chloride extracts: the "blank" is an extract of a copper-EDTA solution that did not contain Gafac, while the "standard" is an extract of the same copper-EDTA solution spiked with Gafac. There is no apparent interference from either the copper or the EDTA.

• *Standards*

Figure 5 is a plot of absorbance versus concentration for a series of Gafac standards. On the basis of previous discussion regarding the apparent variable absorptivity of Gafac, it is not surprising to observe a pronounced curvature in the response curve.

The measured absorbance must necessarily vary with concentration if the supposition holds that micelle formation is influencing the extraction process. The dramatic loss of sensitivity near 200 ppm is probably due to the combined effects of micelle formation and additional factors, such as interactions between Gafac and other species in the solution. In any case, it certainly appears that this determination is best suited to Gafac levels below 170 ppm. Although the response is nonlinear above 20 ppm, careful calibration with several closely spaced standards should make this a usable technique in this concentration range.

The region below 15 ppm is particularly interesting analytically because it is extremely linear and is also the region of highest sensitivity. **Figure 6** provides an enlarged plot of this portion of the calibration curve, together with the calculated 95% confidence band. The confidence band was derived using the procedure described by Natrella [14]. This

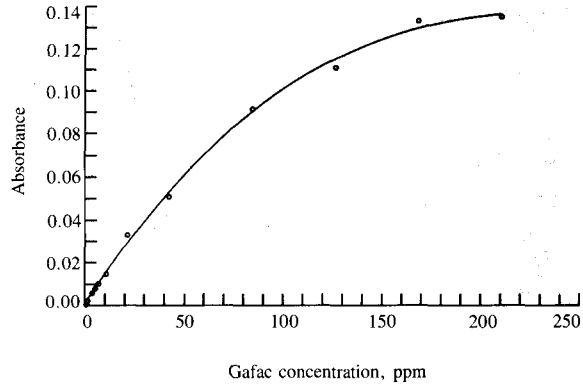


Figure 5

Plot of absorbance versus concentration for methylene chloride extracts of Gafac standards ranging in concentration from 1–210 ppm.

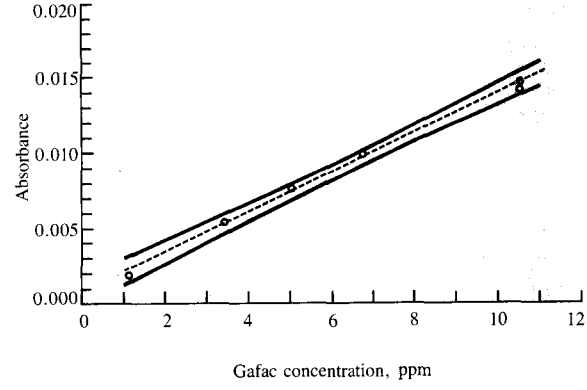


Figure 6

Expanded plot of absorbance versus concentration for methylene chloride extracts of Gafac standards in the concentration range of 1–10.5 ppm. The dashed line represents the best least squares fit to the data. The solid lines denote the upper and lower limits of the 95% confidence band.

confidence band implies that for each absorbance value there is a 95% probability that the Gafac concentration lies between the two extremes defined by the boundaries of the band. As evidenced in this plot, the uncertainty in the Gafac concentration varies from as much as 0.6 ppm at the low and high concentrations to as little as 0.3 ppm at the midpoint.

The question of reproducibility was addressed more rigorously with a separate group of samples. **Table 4** lists the results obtained when ten aliquots of a 10.5-ppm Gafac standard were each extracted and analyzed. Statistically, these data can be reduced as follows:

Table 4 Results of a reproducibility study.

Aliquot no.	*Absorbance* (a.u.)
1	0.0146
2	0.0136
3	0.0131
4	0.0123
5	0.0141
6	0.0176
7	0.0164
8	0.0138
9	0.0123
10	0.0148

$\bar{x} = 0.0143,$
$s = 0.0017.$

Using the calibration curve in Fig. 6 and converting these data to concentration units yields a mean of 10.2 ± 0.6 ppm and a relative standard deviation of 6%.

There is both qualitative and quantitative evidence to suggest a detection limit of less than 1 ppm. Qualitatively, it is observed that a 0.5-ppm standard yields a baseline response. Quantitatively, Eq. (1) can be rearranged and used to calculate a theoretical minimum detectable concentration (c_m):

$$c_m = A/Eb. \quad (7)$$

Substituting $E = 33$, $b = 1.0$ cm, and $A = 0.002$ (twice the observed noise level, which is 0.001 absorbance units) yields a minimum detection limit of 0.6 ppm.

Conclusions

Gafac can be rapidly and reliably determined in complex solution matrices such as copper plating solutions by a combined method utilizing solvent extraction and ultraviolet spectrophotometry. Gafac is first separated from the aqueous solution matrix in three steps:

a. An aliquot of room-temperature solution is acidified to pH 4 with dilute sulfuric acid. This enhances the extractability of Gafac by ensuring that it is in the fully protonated, nonionic form.
b. The pH-adjusted solution is thoroughly contacted with an equal volume of methylene chloride (MC) in a separatory funnel. The aqueous solution and the organic MC are immiscible and form two distinct phases upon standing.
c. The more dense MC phase, containing Gafac, settles to the bottom of the separatory funnel, and the interfering species remain behind in the upper aqueous layer.
d. A few milliliters of the MC extract (from step c) is placed directly in a quartz cuvette and the ultraviolet absorbance is measured at 276 nm relative to an MC blank.
e. Using a suitable calibration curve or the method of standard additions, a Gafac concentration can be determined for the original sample.

The actual analysis of Gafac, after it has been separated from interfering chemical species, is quite simple:

Quantitation is dependent upon inherently nonlinear calibration curves which must be carefully constructed and limited to narrow concentration ranges.

Acknowledgments

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Steven A. Schubert *IBM Systems Technology Division, 1701 North Street, Endicott, New York 13760.* Dr. Schubert is presently a staff engineer in the Additive Plating Department of advanced circuit packaging manufacturing engineering. Since joining IBM in 1981, he has been involved in studying electroless copper plating processes. Previously he worked at Procter & Gamble, Cincinnati, Ohio, developing analytical methods for new products, and at the Radian Corporation, Austin, Texas, researching new techniques for examining coal-fired power plant emissions, secondary aerosol formation, and atmospheric pollutants. He earned a B.S. in chemistry from Humboldt State University, Arcata, California, in 1976 and a Ph.D. in analytical chemistry from the University of Arizona, Tucson, in 1980. His graduate work, supported in part by an American Chemical Society fellowship and the Carl S. Marvel Fellowship, involved applied research in areas dealing with synthetic inorganic mechanisms, acid rain, and sulfur speciation. Dr. Schubert is a member of Alpha Chi Sigma, the American Chemical Society, and the American Electroplaters' Society.