Continuous autoanalyzer for the evaluation of the exhaustion of industrial degreasing baths based on the determination of total grease and surfactant contents

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Abstract

A continuous flow autoanalyzer for at-line monitoring of total grease and surfactant contents in alkaline degreasing baths is proposed. For this purpose, a simple, robust, automated configuration has been on-line coupled to an universal response detector, such as the evaporative light scattering one. The proposed autoanalyzer constitutes an advantageous alternative to manual procedures and achieves the determination of both indices in ca. 15 min. The parameters thus obtained can be used to evaluate the degree of exhaustion of the bath as therefore allows the timely decision-making about reusability, maintenance or renewal. The fractionation model has been validated using attenuated total reflection-Fourier transform-infrared (ATR-FT-IR) spectroscopy. The potential of the method was realized by applying it to the analysis of 15 real samples obtained from precleaning and cleaning alkaline baths from a production line of a metal industry.
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1. Introduction

Some industries related to metal fabrication and finishing or surface coating, use oils and greases during the manufacturing or processing as lubricants or cooling agents. These compounds have to be eliminated from the final product and therefore, sequential cleaning processes are used for this purpose. Until the mid-1980s, the traditional cleaning practices involve the use of organic chlorinated solvents such as trichloroethane or trichloroethylene. After being demonstrated that these substances are risky for environment (contributing to the depletion of the ozone layer) and humans (carcinogenic), aqueous-base alternatives were proposed by environmental bodies [1]. The alternatives were semi-aqueous [2] (with low percentage of organic compound, such as glycol esters) and aqueous [3,4] cleaners.

Aqueous cleaners can be classified depending on their acid/basic properties, in three subcategories: acid, neutral or alkaline cleaners. Alkaline [5] cleaners are by far the most used, and comprise of a mixture of three different main products, namely alkalinity builders, surface active agents and water conditioners. Alkaline builders neutralize the acidic contaminants producing grease saponification. The selection of the alkaline products depends on the level of cleanness required being sodium and potassium hydroxide frequently used. Other alternatives, like silicates, can be also useful. Surface active agents (mainly non-ionic and anionic surfactants) reduce the surface tension of water, enhancing the penetration of the cleaner, and also stabilize the grease in the degreasing bath, creating an emulsion. These surface agents are usually a mixture of different surfactants rather than a pure, single compound. Water conditioners (chelators) are used to inhibit the action of undesirable ions. Finally, corrosion inhibitors can also be added to the bath.

Monitoring the exhaustion of the degreasing bath, in terms of grease and surfactant concentration, is an essential issue for achieving all these purposes. In some laboratories, these parameters are determined following a modified Environmental Protection Agency (EPA) gravimetric method [6]. It is tedious and time consuming and negatively affects the productivity related properties with the subsequent delay in decision-making. Due to

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recent legal restrictions about waste discharge, industry efforts have been focused on the development of different alternatives for reducing the amount of waste aimed at recycling the cleaning products. In this regard, closed-loop [7,8] aqueous cleaning technologies have been introduced in some industries, being ultrafiltration [9] the methodology of choice for extending the degreasing bath useful lifetime.

In this work, a simple and automated method for the determination of the degree of exhaustion of industrial degreasing baths is proposed based on the determination of the total grease and surfactant contents. The optimized procedure avoids manual sample treatment, such as liquid–liquid extraction and emulsion breakage. The universal response provided by the evaporative light scattering detection (ELSD) [10] permits also the replacement of the gravimetric measurement. Under these conditions, the two families of compounds are quantitatively retained on the sorbent and selective, sequential elutions were performed using proper solvents. The method provides results in only ca. 15 min using a single sample aliquot.

2. Experimental

2.1. Apparatus

The flow system used is schematically depicted in Fig. 1. It consists of a Hewlett-Packard 1050 high pressure quaternary pump for solvents (water, acetonitrile, ethyl acetate and methanol) delivery; a high pressure injection valve (Rheodyne 7725, Cotati, CA) fitted with a 250 μl PTFE sample loop and a DDL 31 evaporative light scattering detector (Eurosep, Cergy-Pontoise, France) for analytes determination. The temperature of the ELSD evaporation chamber was fixed at 65 °C, using compressed air (Air Liquide, Seville, Spain) as nebulizing gas. Photomultipler gain was set at 550 and 450 V depending on the analyte and was changed during the analysis. The sample loop was filled by means of a glass syringe. PTFE tubing of 0.5 mm I.D. for coils, and standard connectors were also employed. The flow system was connected to the ELSD by means of a 50 cm × 0.1 mm I.D. Poly-ether-ether-ketone (PEEK) tubing. For analytes retention, a laboratory-made Strata X column was constructed by packing 40 mg of the sorbent into a 3 cm × 4 mm I.D. PTFE tube using beads of cotton wool to prevent material losses. Signals were acquired using HPChem Station software (Agilent Technologies) interface via an HP 35900C A/D converter. Peak area for surfactant and peak height for oil were used as analytical signal.
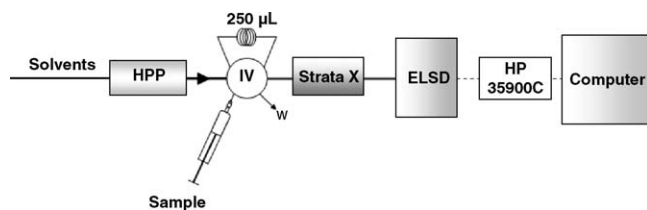

Fig. 1. Schematic diagram of the continuous flow configuration designed for the sequential determination of total grease and surfactant contents in degreasing bath samples.

To corroborate the composition of the two analytical signals obtained with the ELSD, a Bruker Tensor37 Fourier transform-infrared (FT-IR) spectrometer, equipped with a diamond attenuated total reflection (ATR) cell with a circular surface of 3 mm diameter and three internal reflections was employed. A liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector was used for spectra acquisition between 4000 and 600 cm^{-1} at a 4 cm^{-1} resolution with 128 co-added scans each. Data collection and processing was made using OPUS software (Bruker, Ettligen, Germany). A spectrum of the dry ATR surface was used as background.

2.2. Reagents and samples

All solvents were of analytical grade or better. HPLC gradient grade acetonitrile, ethyl acetate and methanol were supplied by Scharlau (Barcelona, Spain). Light mineral oil was purchased from Sigma–Aldrich (Madrid, Spain). Commercial degreasing products Ridoline 1565-1 (alkaline degreasing agent containing between 5 and 15% of phosphate and >10% of sodium hydroxide) and Ridosol HI 1808 (moistening for alkaline degreasing containing between 15 and 30% of non ionic surfactants) were kindly supplied by Henkel-Technologies (Barcelona, Spain).

Strata X sorbent was obtained from Phenomenex (Jasco Analítica, Madrid, Spain). It is a polymeric reversed phase sorbent with a high surface area (>700 m^2 g^{-1}) and 33 μm particles, which provides high capacity and high extraction efficiency.

A total of 15 alkaline degreasing bath samples, were supplied by Henkel Technologies. Real samples were filtered through paper in a vacuum manifold to prevent solid particles to be introduced into the autoanalyzer.

2.3. Reference method

The reference method for oil and surfactant determination in alkaline degreasing baths consists of a liquid–liquid extraction of the analytes from the aqueous matrix with n-hexane followed by gravimetric determination of both parameters. For this purpose, aliquots of 250 ml of sample are placed in an extraction funnel and 50 g of magnesium sulfate and 5–10 ml of sulfuric acid were added. Then, 50 ml of n-hexane were added and the mixture was shaken and allowed to settle. The aqueous phase is discarded and the process is repeated twice with fresh organic solvent. The whole organic phase is then transferred to a baker previously weighted which is introduced in an oven (70–80 °C) for solvent evaporation, the residue is weighed (P1) and corresponds to the total sum of surfactants and grease present in the sample. This oily residue is redissolved in 50 ml of n-hexane and the solution is passed through a silica gel sorbent. The eluate is collected and dried up again in an oven obtaining a residue (P2), which corresponds to the total grease content. The surfactant is calculated by subtraction (P2 − P1).

2.4. Autoanalyzer functioning

The autoanalyzer designed for analytes monitoring operates in a sequential fashion. Initially, the loop of the high-pressure