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Determination of aluminum rolling oil additives and contaminants using infrared spectroscopy coupled with genetic algorithm based multivariate calibration

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ABSTRACT

Genetic algorithm based multivariate calibration models were generated for infrared spectroscopic determination of aluminum rolling oil additives and contaminants such as gear and hydraulic oils. Two different additives and six different suspected contaminants were investigated in the base oil lubricant. Routine analysis samples from 9 different aluminum rolling systems were collected in a period of 2 months in an aluminum rolling plant and gas chromatography (GC) is used as the reference method. Infrared absorbance spectra of the samples were then collected and the reference values obtained with GC were used together with these spectra for model building. Inverse least squares method was optimized with a genetic algorithm by selecting the most contributing regions of the infrared spectra for each component. The R^2 values between GC and multivariate spectroscopic determinations were around 0.99 indicating a good correlation between the two methods. Performance of genetic algorithm based multivariate calibration models were also compared with partial least squares (PLS) method. The study showed that infrared spectroscopy coupled with multivariate calibration can be used for continuous monitoring of additives and contaminants in aluminum rolling oil. By this way, analysis time is significantly reduced and simultaneous determination of all the components can be accomplished.

1. Introduction

Common machinery oils for lubricating hydraulic systems, gear box or bearings of sheet and foil mills are composed of mineral or synthetic oils with a number of additives such as extreme pressure additives, friction modifiers, corrosion inhibitors, oxidation inhibitors, viscosity modifiers, pour point depressants, foam decomposers, etc. The additives are very important in order to improve the performance of machinery oils in operation. The concentration of the additives may vary significantly from 1–2% to 30%, depending on the requirement [1]. These oils and additives must be non-staining and complied with food codex as the aluminum foils produced in foil mills were consumed in many food packaging applications without any further cleaning other than heat treatment of the aluminum plates and foils in order to remove residues of rolling oils and additives. On the other hand, the lubrication and cooling oil mixture were sprayed as fine droplets to the rolling mills and unavoidably these oils were contaminated to some extent with gear and hydraulic fluids of the rolling machines since the solubility of these fluids were quite high in rolling oils. The chemical characteristics of the contaminants are very much different from rolling oils and often have higher boiling points and this causes serious staining problems that can not be removed with heat treatment of the finished products resulting in significant profit loses for the industry. In addition, undesired mixing of gear and hydraulic fluids with rolling oils change the lubricating performance of the oil mixtures resulting in mechanical deformations on the rolled sheets and foils [2].

Several analytical methods were proposed in the literature for analysis of complex industrial oil blends. High performance liquid chromatography (HPLC) was used to determine contamination of cold rolling oils with hydraulic fluids and gear oils [1]. In a comparative study, synthetic esters that are used in aluminum hot rolling lubricants were determined using chromatographic and titrimetric methods and results were compared based on the acid number and hydroxyl number [3]. Bernabei et al. [4] described two gas chromatography (GC) based methods for the determination of additives that are found in lubricating oils used in gas turbine engines. In another study, identification and quantitative determination of contaminants in lubricating and hydraulic fluids were reported by using gas chromatography weight-spectrometry [5]. Haveng and Rohwer [6] reported the application of capillary gas chromatography to rapid screening of rolling mill oils.

However these chromatographic techniques suffer from long analysis times and if several rolling mills are to be monitored continuously these techniques are not very practical for routine

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analysis. Spectroscopic analysis is an alternative to chromatographic methods in terms of rapid analysis and relatively cheap operation costs along with on-line monitoring advantages. For example, Paschoal and et al. [7] had used near infrared spectroscopy coupled with a multivariate partial least squares calibration (PLS) method for their analysis of contaminants in lubricating oils. Gasoline, ethylene glycol and water contamination in automotive engine lubricating oils were determined using attenuated total reflectance (ATR) mid infrared spectroscopy and PLS [8]. Fluorescence spectroscopy was used to determine tramp oil contaminations in hot rolling oil emulsions [9]. Synchronous fluorescence measurements were made with a fluorescence tracer in order to enhance the contaminant signal and distinguish it from rolling oil signal. Fourier transform infrared (FTIR) spectroscopy combined with multivariate calibration was used to monitor lubricating oil degradation and analysis of possible contaminants in aluminum cold rolling systems [10–12]. A recent study focused on different modes of FTIR spectroscopy for the determination of organic monolayers of lubricating oil residues on the surface of rolled aluminum sheets after heat treatment [13]. The authors proposed a surface enhanced infrared spectroscopic method for the effective determination of thin organic films on the surfaces of aluminum sheets.

Multivariate calibration methods make it possible to relate instrument responses that consist of several predictor variables to a chemical or physical property of a sample. Several classical multivariate calibration methods have been developed in last couple of decades [14–16] for the analysis of complex chemical mixtures, and the choice of the most suitable calibration method is very important in order to generate calibration models with high predictive ability for future samples. In some cases, conventional methods may not offer a satisfactory solution to a given problem due to the complexity of the data, and it may be necessary to apply some sort of variable selection. There have been many mathematical methods of variable selection and genetic algorithm is one of them offering a fast and effective solution for large scale problems [17–20]. Inverse least squares (ILS) is based on the inverse of Beer's Law, where concentrations of an analyte are modeled as a function of absorbance measurements. Genetic inverse least squares (GILS) is a modified versions of original ILS method in which a small set of wavelengths are selected from a full spectral data matrix and evolved to an optimum solution using a genetic algorithm (GA), and has been applied to a number of wavelength selection problems. The detailed description of the GILS algorithm has been given in number of recent studies [21–23].

In this study, the determination of additives and possible contaminants, such as gear and hydraulic oils in aluminum rolling oils is presented with the aim of developing a fast and reliable FTIR spectroscopic method for the routine analysis of industrial aluminum rolling systems. The conventional analysis method that is in practice in the particular industrial aluminum sheet and foil plant is based on a capillary column GC and suffers form long analysis times. As a result, it becomes too late to act on the contamination prevention resulting in unacceptable product and loss of profit. The proposed FTIR based spectroscopic method is much faster for determination of the concentrations of the additives and possible contaminants in the aluminum rolling oils. The GILS method was used as the multivariate calibration and wavelength selection method for each component of the lubricating oil mixtures. In addition to GILS, partial least squares (PLS) is also used to build calibration models in order to determine possible improvements offered by genetic algorithm based approach.

1.1. Genetic inverse least squares

The major drawback of the classical least squares (CLS) method is that all of the interfering species must be known and their concentrations included in the model. This need can be eliminated by using the inverse least squares (ILS) method which uses the inverse of Beer's Law. In the ILS method, concentration of a component is modeled as a function of absorbance measurements. Because modern spectroscopic instruments are very stable and provide excellent signal-to-noise (S/N) ratios, it is believed that the majority of errors lie in the reference values of the calibration sample, not in the measurement of their spectra. In fact, in many cases the concentration data of calibration set is generated from another analytical technique that already has inherent errors which might be higher than those of the spectrometer (for example, Kjeldahl protein analysis used to calibrate NIR spectra).

The ILS model for m calibration samples with n wavelengths for each spectrum is described by:

$$\mathbf{C} = \mathbf{AP} + \mathbf{E_C} \tag{1}$$

where $\mathbf{C}$ is the $m \times l$ matrix of the component concentrations, $\mathbf{A}$ is the $m \times n$ matrix of the calibration spectra, $\mathbf{P}$ is the $n \times l$ matrix of the unknown calibration coefficients relating l component concentrations to the spectral intensities and $\mathbf{E_C}$ is the $m \times l$ matrix of errors in the concentrations not fit by the model. In the calibration step, ILS minimizes the squared sum of the residuals in the concentrations. The biggest advantage of ILS is that Eq. (1) can be reduced for the analysis of single component at a time since analysis is based on an ILS model is invariant with respect to the number of chemical components included in the analysis. The reduced model is given as:

$$\mathbf{c} = \mathbf{Ap} + \mathbf{e_c} \tag{2}$$

where $\mathbf{c}$ is the $m \times 1$ vector of concentrations for the component that is being analyzed, $\mathbf{p}$ is $n \times 1$ vector of calibration coefficients and $\mathbf{e_c}$ is the $m \times 1$ vector of concentration residuals not fit by the model. During the calibration step, the least-squares estimate of $\mathbf{p}$ is:

$$\hat{\mathbf{p}} = (\mathbf{A}'\mathbf{A})^{-1}\mathbf{A}' \cdot \mathbf{c} \tag{3}$$

where $\hat{\mathbf{p}}$ are the estimated calibration coefficients. Once $\hat{\mathbf{p}}$ is calculated, the concentration of the analyte of interest can be predicted with the equation below.

$$\hat{c} = \mathbf{a}' \cdot \hat{\mathbf{p}} \tag{4}$$

where $\hat{c}$ is the scalar estimated concentration and $\mathbf{a}$ is the spectrum of the unknown sample. The ability to predict one component at a time without knowing the concentrations of interfering species has made ILS one of the most frequently used calibration methods.

The major disadvantage of Eq. (3) is that the number of wavelengths in the calibration spectra should not be more than the number of calibration samples. This is a big restriction since the number of wavelengths in a spectrum will generally be much more than the number of calibration samples and the selection of wavelengths that provide the best fit for the model is not a trivial process. Several wavelength selection strategies, such as stepwise wavelength selection and all possible combination searches are available to build a model which fits the data best.

Genetic Algorithms (GA) are global search and optimization methods based upon the principles of natural evolution and selection as developed by Darwin. Computationally, the implementation of a typical GA is quite simple and consists of five basic steps including initialization of a gene population, evaluation of the population, selection of the parent genes for breeding and mating, crossover and mutation, and replacing parents with their offspring. These steps have taken their names from the biological foundation of the algorithm.

Genetic inverse least squares (GILS) is an implementation of a GA for selecting wavelengths to build multivariate calibration

models with reduced data set. GILS follows the same basic initialize/breed/mutate/evaluate algorithm as other GA's to select a subset of wavelengths but is unique in the way it encodes genes. A gene is a potential solution to a given problem and the exact form may vary from application to application. Here, the term gene is used to describe the collection of instrumental response at the wavelength range given in the data set. The term 'population' is used to describe the collection of individual genes in the current generation.

In the initialization step, the first generation of genes is created randomly with a fixed population size. Although random initialization helps to minimize bias and maximize the number of possible recombinations, GILS is designed to select initial genes in a somewhat biased random fashion in order to start with genes better suited to the problem than those that would be randomly selected. Biasing is done with a correlation coefficient by plotting the predicted results of initial population against the actual component concentrations. The size of the gene pool is a user defined even number in order to allow breeding of each gene in the population. It is important to note that the larger the population size, the longer the computation time. The number of instrumental responses in a gene is determined randomly between a fixed low limit and high limit. The lower limit was set to 2 in order to allow single point crossover whereas the higher limit was set to eliminate over fitting problems and reduce the computation time. Once the initial gene population is created, the next step is to evaluate and rank the genes using a fitness function, which is the inverse of the standard error of prediction from cross validation (SEPCV).

The third step is where the basic principle of natural evolution is put to work for GILS. This step involves the selection of the parent genes from the current population for breeding using a roulette wheel selection method according to their fitness values. The goal is to give a higher chance to those genes with high fitness so that only the best performing members of the population will survive in the long run and will be able to pass their information to the next generations. Because of the random nature of the roulette wheel selection method, however, genes with low fitness values will also have some chance to be selected. Also, there will be genes that are selected multiple times and some genes will not be selected at all and will be thrown out of the gene pool. After the selection procedure is completed, the selected genes are allowed to mate top-down in pairs whereby the first gene mates with the second gene and the third one with the fourth one and so on as illustrated in the following example:

Parents

$$S_1 = (A_{1147}, A_{951}, \#A_{2179}, A_{2218}) \quad (5)$$

$$S_2 = (A_{1225}, A_{1478}, \#A_{1343}, A_{950}, A_{1451}, A_{2358}, A_{931}, A_{1158}) \quad (6)$$

The points where the genes are cut for mating are indicated by #.

Offspring

$$S_3 = (A_{1147}, A_{951}, A_{1343}, A_{950}, A_{1451}, A_{2358}, A_{931}, A_{1158}) \quad (7)$$

$$S_4 = (A_{2179}, A_{2218}, A_{1225}, A_{1478}) \quad (8)$$

where $A1147$ represents the instrument response at the wavelength given in subscript, S_1 and S_2 represent the first and second parent genes and S_3 and S_4 are the corresponding genes for the offspring. Here the first part of S_1 is combined with the second part of the S_2 to give the S_3, likewise the second part of the S_1 is combined with the first part of the S_2 to give S_4. This process is called the single point crossover and is common in GILS. Single point crossover will not provide different offspring if both parent genes are identical, which may happen in roulette wheel selection, when both genes are broken at the same point. Also note that mating can increase or decrease the number of instrument responses in the offspring genes. After crossover, the parent genes are replaced by their offspring and the offspring are evaluated. The ranking process is based on their fitness values following the evaluation step. Then the selection for breeding/mating starts all over again. This is repeated until a predefined number of iterations are reached.

Mutation which introduces random deviations into the population was also introduced into the GILS during the mating step at a rate of 1% as is typical in GA's. This is usually done by replacing one of the responses in an existing gene with a randomly selected new one. Mutation allows the GILS to explore the search space and incorporate new material into the genetic population. It helps keep the search moving and can eject GILS from a local minimum on the response surface. However, it is important not to set the mutation rate too high since it may keep the GA from being able to exploit the existing population. Also, the GILS method is an iterative algorithm and therefore there is a high possibility that the method may easily over fit the calibration data so that the predictions for independent sets might be poor. To eliminate possible over fitting problems, cross validation is used in which one spectrum is left out of the calibration set and the model is constructed with $m-1$ sample. Then this model is used to predict the concentration of left out sample. This process is continued until all samples are left out al least once in each iteration. As long as the number of spectra in the calibration set is not too large, cross validation is an effective method of eliminating over fitting. If the number of calibration spectra is very large, then the GILS method has the option of half validation approach in which the half of the spectra in the calibration set is used to validate the model in each iteration.

In the end, the gene with the lowest SEPCV (highest fitness) is selected for the model building and this model is used to predict the concentrations of component being analyzed in the prediction (test) sets. The success of the model in the prediction of the test sets is evaluated using standard error of prediction (SEP). Because random processes are heavily involved in GILS as in all the GA's, the program has been set to run several times for each component in this study. The best run (i.e. the one generating the lowest SEPCV for the calibration set) is subsequently selected for evaluation and further analysis. The termination of the algorithm can be done in many ways. The easiest way is to set a predefined iteration number for the number of breeding/mating cycles.

GILS is relatively simple in terms of the mathematics involved in the model building and prediction steps, but at the same time it has the advantages of the multivariate calibration methods with a reduced data set since it uses the full spectrum to extract genes. By selecting a subset of instrument responses it is able to minimize nonlinearities that might be present in the full spectral region.

2. Experimental

2.1. Materials

Aluminum rolling oil, additives, hydraulic oils and gear oils were purchased from different suppliers. The rolling base oil named as Linpar 13–14 which is linear paraffinic oil with 13–14 carbon chain length was obtained from Sasol (Sasol Italy S.p.A. Milano, Italy). The additive Nafol 1214S is a blend of linear alcohols with 10–16 carbon chain length and used as antioxidant and wetting agent. It is also supplied by Sasol, Italy. Another additive that was used in this study is Cindolube SR 99 AP which is purchased from Houghton (Houghton Italia S.p.A, Genova, Italy). Cindolube SR is a performance additive lubricant used as antioxidant and wetting agent.

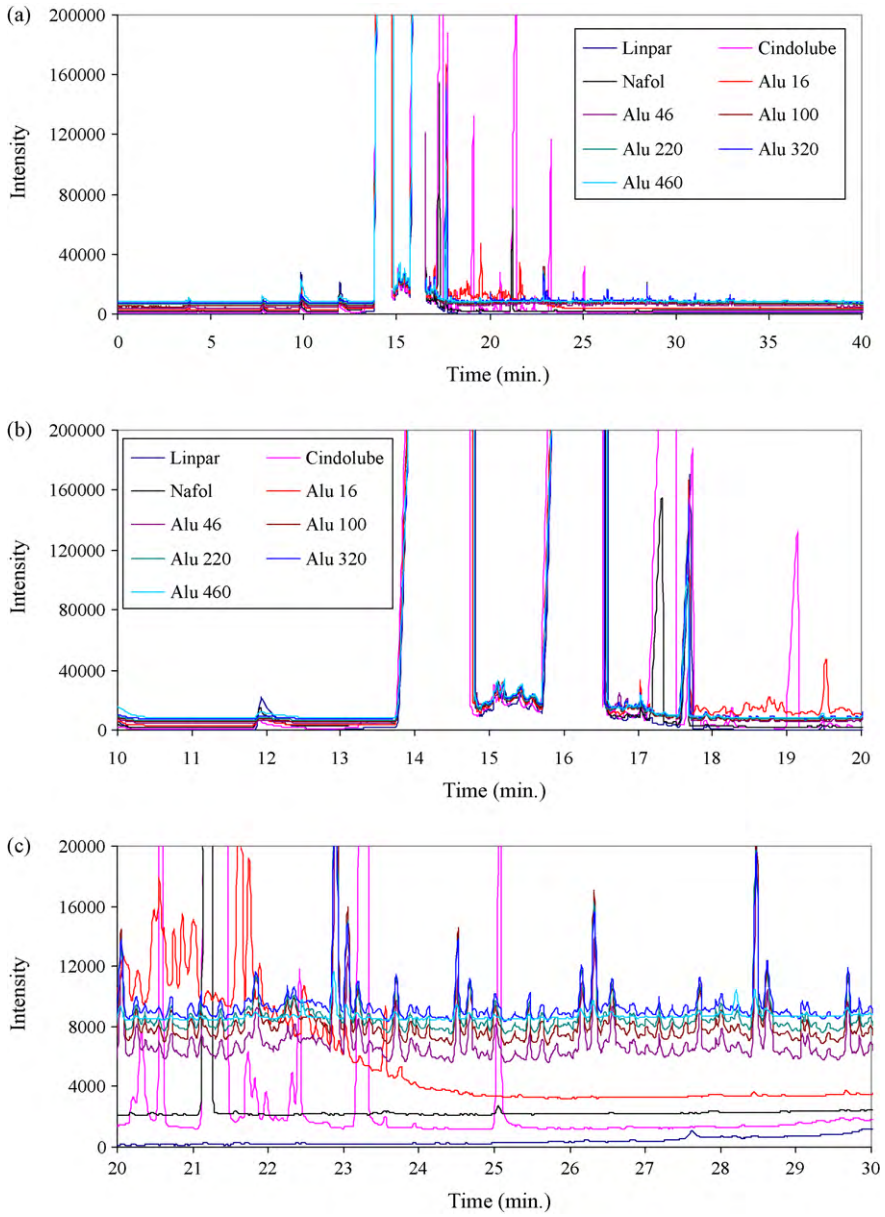

Fig. 1. GC chromatograms of aluminum rolling base oil, additives, hydraulic and gear oils. (a) Complete chromatograms, (b) between 10 and 20 min, and (c) between 20 and 30 min.

Hydrotex Alu 16 and 46 (Belgin Madeni Yağlar Ticaret Ve Sanayi A.Ş., Kocaeli, Turkey) were used in the aluminum rolling mills as the hydraulic oils. A number of gear oils were also investigated in this study as the possible source of contaminations in aluminum rolling lubricating oils. Among them, Recompound Alu 100, 220, 320 and 460 that are also purchased from Belgin, were used in this study.

2.2. Chromatographic analysis

A Shimadzu GC 17A gas chromatography system (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector was used for the reference analysis of real samples taken from the aluminum rolling mills. A fused silica capillary column (Phase bonded, poly 5% diphenyl, 95% dimethylsiloxane) was selected for the analysis of the additives and the hydraulic and gear oils. A gradient temperature program with split mode (1/30) starting from 100 °C with an increment of 5 °C per minute up to 300 °C in the oven for the column were applied in order to separate several peaks for all the components in the chromatograms. Injection port and detector temperatures were set to 280 and 320 °C, respectively. Standard calibration curves were developed for each component in the oil mixture system and reference analysis of the real samples was performed with these calibration models. The reference errors of chromatographic analysis of the components were 0.01% for Nafol, 0.04% for Alu 16, 0.06% for Total Alu and 0.14% for Cindolube by mass (w/w%).

2.3. Spectroscopic analysis

A PerkinElmer Spectrum 100 model FTIR spectrometer (PerkinElmer Inc., MA, USA) were used to collect sample spectra between 4000 and 400 cm^{-1}. This spectrometer was equipped with a KBr beam splitter and fast recovery deuterated triglycine sulfate detector. Samples were measured using rectangular KBr sealed cell,

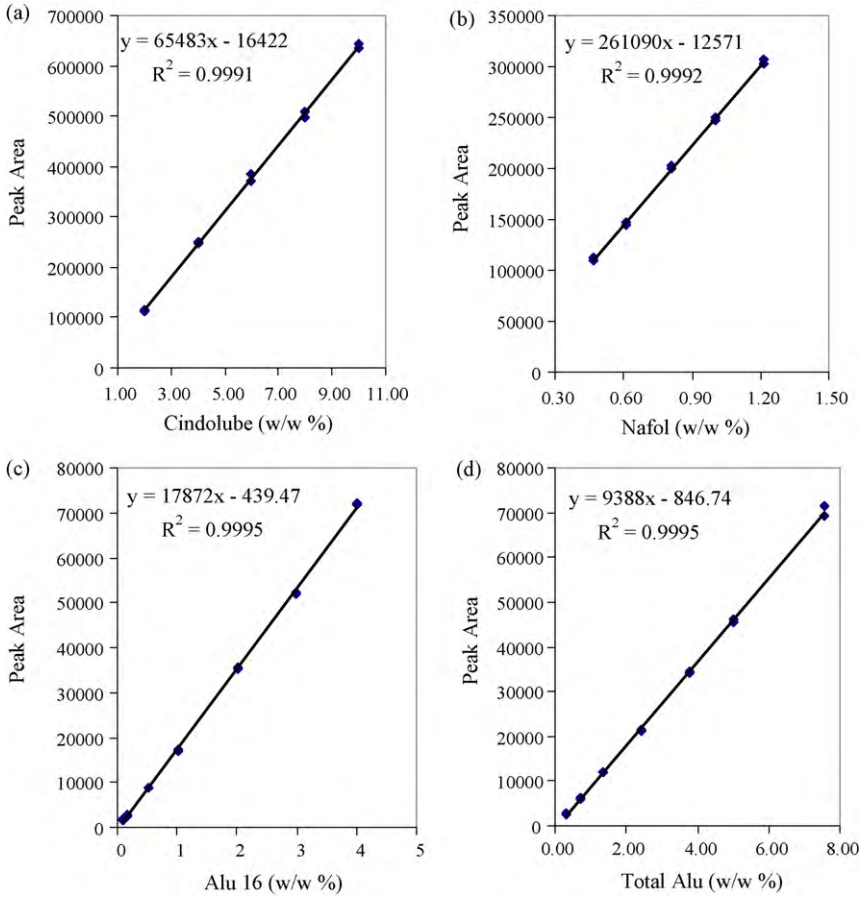

Fig. 2. Standard calibration curves of (a) Cindolube, (b) Nafol, (c) Alu 16, and (d) Total Alu for chromatographic analysis.

with a path length of 0.2 mm and the spectra were collected in absorbance mode by taking Linpar as the background.

2.4. Sample preparation

In order to generate multivariate calibration models, 136 samples of rolling oil samples were collected during a period of 2 months at 9 different rolling systems in the particular aluminum rolling plant. The GC and FTIR analysis of the samples were performed whenever they are collected from different rolling systems in this 2 months period. The rolling systems labeled as C1, C3, FH1, FH2, FH3, and FH4 were designed to be cooled with the base oil Linpar that contained Nafol as the additive and the base oil used in C2, C4, and SH1 rolling systems contained Cindolube as additive. The concentration range of Nafol in the rolling oil ranged from 0.40% to 0.80% by weight whereas the percent concentration of Cindolube was between 4.0% and 8.0% by weight depending on the system. Half of the collected samples contained Nafol as additive and the rest of the samples had Cindolube as additive in the rolling oil.

2.5. Data analysis

Standard GC calibration models were generated on GC instrument described above. Spectra of real samples were then transferred to another computer where all data processing was carried out. The genetic inverse least squares (GILS) method was written in MATLAB programming language using Matlab 5.3 (MathWorks Inc., Natick, MA). As a reference multivariate calibration method, partial least squares (PLS) (Minitab Inc., State College, PA) method was used to compare the performance of GILS.

3. Results and discussion

The additive Nafol 1214S was added to the base oil Linpar up to 0.80% by weight in all the rolling systems in the current aluminum plant where as the percent content of other additive Cindolube SR ranged between 4.0% and 8.0% by weight. Before this study was started, the level of hydraulic and gear oil contaminations were not known quantitatively to the technical staff of the aluminum plant but from the finished products, the existence of residues from these heavier oils were noticed from time to time. This was thought to be the result of contamination of rolling oil as a result of unexpected leaking and dissolving of these heavier oils by base oil. The technical staff have been adding decreased amount of the hydraulic and gear oils to the systems from time to time and dilute rolling oil with fresh base oil as to decrease the contamination effect on the surface of the finished aluminum products. A total of 9 different production lines labeled as C1, C3, FH1, FH2, FH3 and FH4 in which Nafol was the additive in base oil and C2, C4, and SH1 which contained Cindolube as additive in base oil were investigated in this study.

The base oil Linpar was the dominating component in the samples with a percent concentration around 90% and remaining additives and possible contaminants were around 10% maximum. From the initial investigation of chromatograms for the real samples it was seen that Hydrotex Alu and Recompound Alu series gave very low intensity peaks and therefore no further sample dilution was applied prior to GC analysis. The resulting chromatograms con-

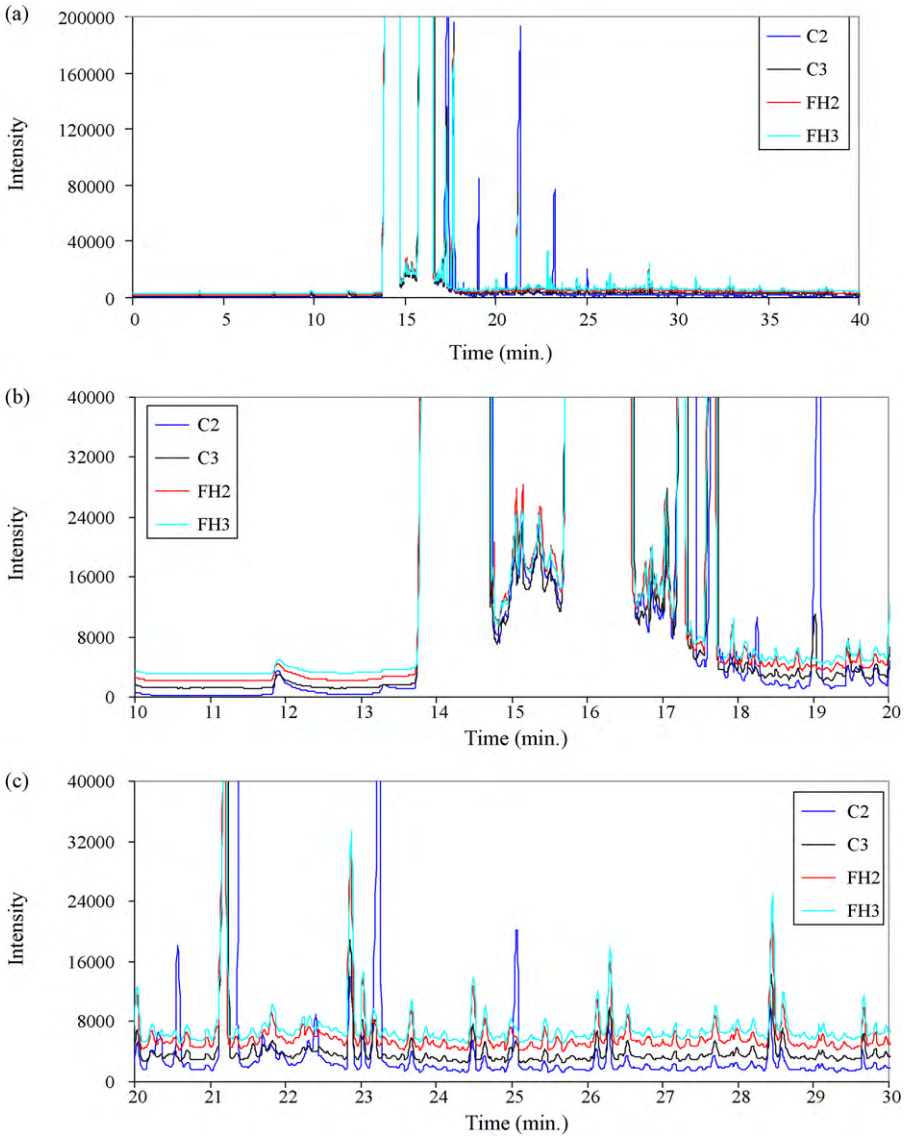

Fig. 3. GC chromatograms of real samples taken from C2, C3, FH2 and FH3 rolling systems. (a) Complete chromatograms, (b) between 10 and 20 min, and (c) between 20 and 30 min.

tained very large and saturated Linpar peaks around 14 and 16 min as shown in Fig. 1. The additives and possible contaminants gave several narrow and small peaks following Linpar peaks. In order to distinguish the chromatographic elution profiles of each additive and possible contaminant, standard calibration samples of these components were prepared in Linpar as weight percent base. As seen from the chromatograms, there is a shift in the intensity scale of each chromatogram which was artificially made by adding a gradually increasing constant (e.g. an offset of 1000 was added to second and 2000 for the third one and so on) to each chromatogram. Because the full chromatogram takes 40 min and contains closely spaced several peaks, the regions where the additives and possible contaminants gave peaks were enlarged in two separate graphs one between 10 and 20 min and other between 20 and 30 min. The two peaks around 17.35 min belong to additives Cindolube and Nafol. Here the larger one was resulted from Cindolube as its standard concentration is almost 10 times when compared with the standard of Nafol in Linpar. These peaks are used to quantify Cindolube and Nafol in real samples. Note that the additives Nafol and Cindolube gave very similar chromatograms and there was no distinguishable peak for Nafol from Cindolube whereas Cindolube had a number of other unique peaks after 19th minute. Since the real sample did not contain Nafol and Cindolube at the same time in the real samples, it was still possible to analyze these components for the different aluminum rolling systems.

When compared with other Alu components, it was possible to separate hydrotex Alu 16. As seen from the middle chromatogram in which the retention times between 10 and 20 min are shown, the Alu 16 gave a unique peak around 19.50 min. Also the peak around 21.50 min belongs to the Alu 16 shown in the bottom chromatogram. Both of these peaks are used to develop calibration models for Alu 16 and the one that is observed at 21.50 min were used for the quantification of this component in the real samples. On the other hand, retention times between 20 and 30 min shown on the bottom chromatogram indicated several peaks for Hydrotex A1u 46 and Recompound Alu series (Alu 100, 220, 320 and 460) and all of these peaks are the same in each of these components. Several different GC programs were tested with the hope of separating these components but except the Alu 16, all others gave almost the same chromatograms in all these trials. As a result, it was not possible to obtain reference GC analysis for each of these components. Therefore, determination of total contamination due to these components (except Alu 16) was carried out by preparing a mixture stock solution of these standards which contained equal

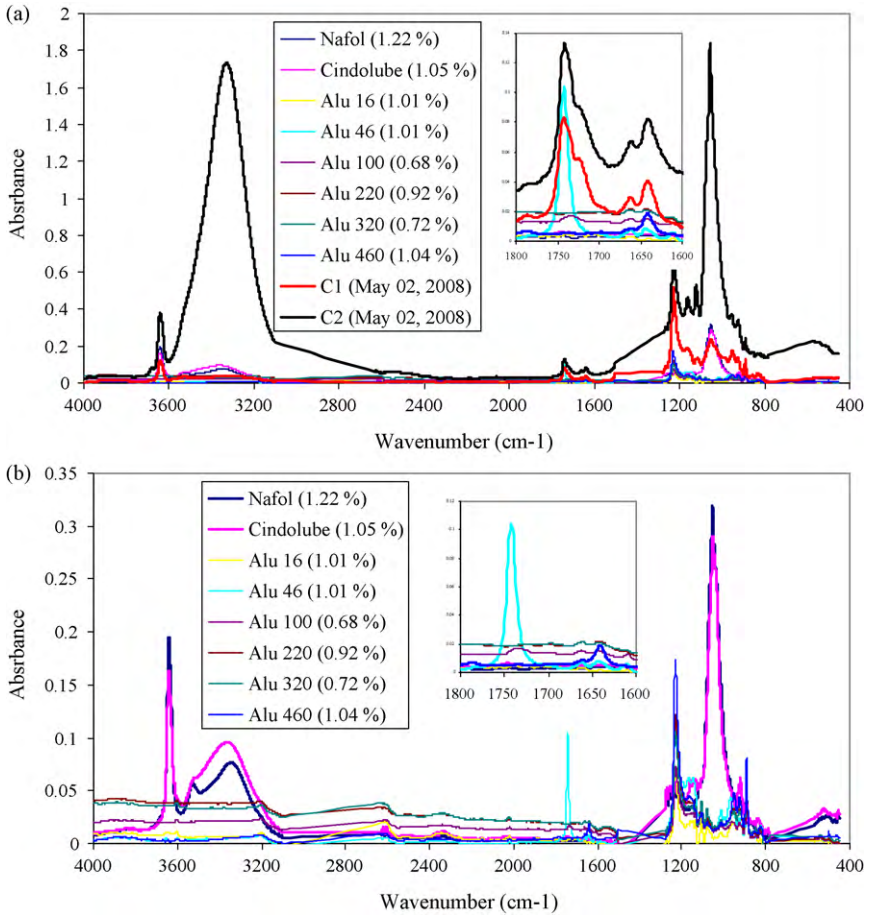

Fig. 4. FTIR spectra of pure components along with two real samples between 4000 and 400 cm^{-1} wavenumbers. (a) With the real samples and (b) without the real samples.

amount from each one of them. Among the several peaks observed for the Alu mixtures, the peak around 22.90 min were used to quantify total Alu in the real samples. Standard calibration solutions of Cindolube (0.50–10.0%, w/w), Nafol (0.40–1.20%, w/w), Alu 16 (0.10–4.0%, w/w), and total Alu (0.20–8.0%, w/w) were prepared in Linpar. Duplicate analysis of these standard were carried out for each component in order to make sure that the reproducibility of the chromatographic analysis is approached and simple calibration models were constructed by using the peak areas at the selected retention times. Fig. 2 shows standard calibration curves for Cindolube, Nafol, Hydrotex Alu 16 and total Alu (Alu 46, 100, 220, 320, and 460). The linearity of standard calibration curves for all the component were quite good as shown in Fig. 2 and they were used to determine Cindolube, Nafol, Alu 16 and total Alu in the real samples collected from Aluminum rolling systems in a period of 2 months routine sample collection. Duplicate analysis of the real samples was also performed and average of these determinations was used as the reference data for further spectroscopic analysis. Representative chromatograms of real samples that are taken from C2, C3, FH2 and FH3 production lines are shown in Fig. 3. As indicated before, there were 9 different rolling systems including sheet and foil rolling lines but for the sake of clarity only four of them are displayed here. As seen from Fig. 3, the small peaks around 19.50 and 21.50 min indicate that the presence of Hydrotex Alu 16 is very low in the real samples. On the other hand, total alu components gave a number of peaks especially after 20 min retention times. The reason for the three Nofol system chromatograms that were illustrated in this figure is that FH2 and FH3 systems had high amount of total Alu contamination relative to any other system investigated here. The results of the additives, total Alu components and Alu 16 and other components in real samples will be given later in the following section as a comparison with multivariate spectroscopic analysis results.

After completing chromatographic analysis of the standard and real samples that would be included in the spectroscopic calibration models, FTIR spectra of the same samples were collected. Fig. 4 shows the FTIR pure component spectra of the additives and possible contaminants along with real samples. These spectra were obtained against pure base oil Linpar background. The upper graph shows all the pure components with a percent concentration around 1.0% (w/w) in Linpar and two real samples one from the Nafol systems (C1) and the other from the Cindolube systems (C2). The bottom graph is obtained after removing real samples from the above graph as C1 and especially C2 samples have much intense peaks that hide the features of the other components. As seen from bottom graph, the Alu 46 has a very sharp peak around 1740 cm^{-1} and in fact, none of other components studied here gave a peak at this wavenumber. Existence of this peak in the real samples can be clearly seen in the samples from C1 and C2 rolling systems. Therefore, a preliminary conclusion can be made at this moment for a possible Alu 46 contamination. In addition to Alu 46 contamination, the presence of Alu 460 in the real samples is evident form the upper graph as seen from the enlarged region between 1600 and 1800 cm^{-1}. Here the peak around 1640 cm^{-1} is clearly due to Alu 460 in real samples.

When the pure component spectra of other Alu series (Alu 16, Alu 100, 220, and 320) are examined it is seen that they all gave some peaks around 900 and 1200 cm^{-1} regions but these peaks are all overlapped with not only themselves but also with the Nafol and Cindolube peaks. For this reason it is not easy to state directly

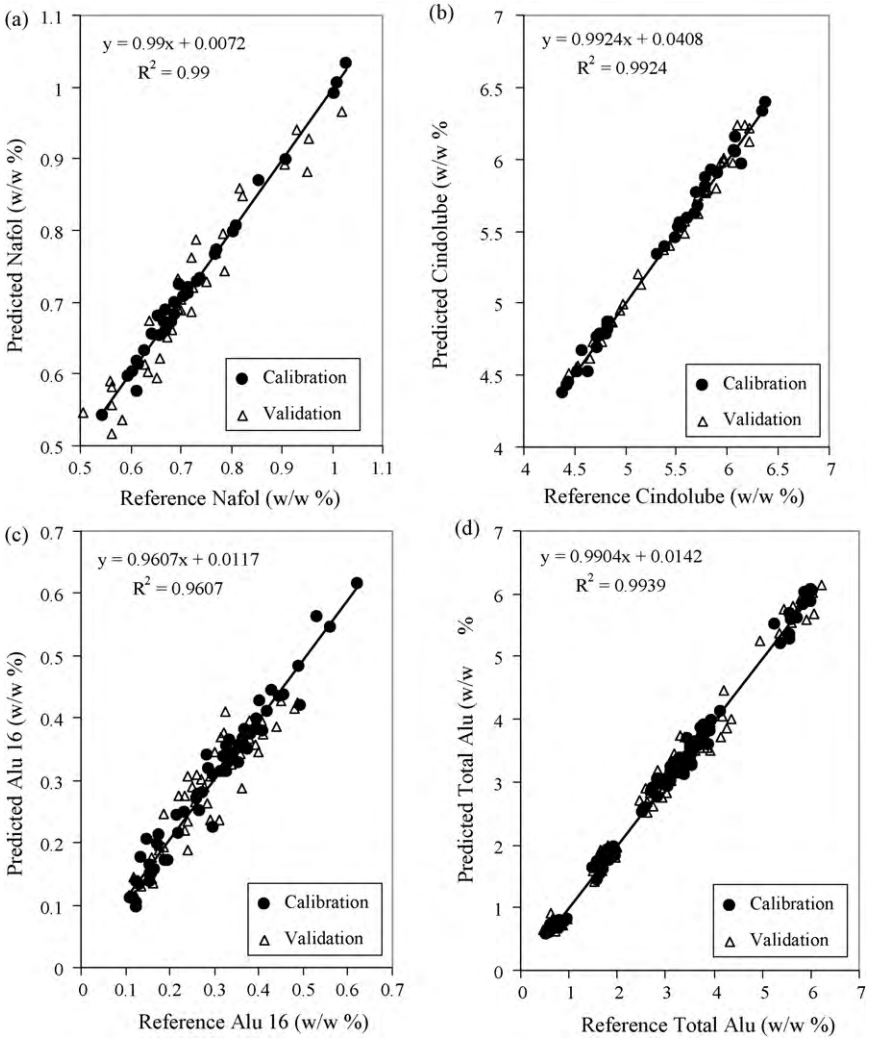

Fig. 5. Reference values obtained from GC analysis vs. GILS predictions based on FTIR spectra for the additives (a) Nafol and (b) Cindolube and for the contaminants (c) Alu 16, and (d) Total Alu contents.

from these spectra whether if there is a contamination due to these components or Nafol and Cindolube in the real samples. This would be answered only after developing multivariate calibration models for each of these components. However, from the chromatographic analysis of these components it was clear that Alu 16 can be separated from others (Alu 46, Alu 100, 220, 320, and 460). Therefore chromatographic analysis will eventually let us know if there is a contamination due to Alu 16. On the other hand, as mentioned before, the presence of Alu 46, Alu 100, 220, 320 and 460 can only be reported as total amount due to these components in the real samples based on chromatographic analysis.

Even though it was possible to generate multivariate calibration models using synthetically prepared mixtures for the Alu components that were not separated by chromatographic analysis, this study was planned to focus on multivariate modeling of the components that were successfully separated by the GC analysis. Therefore individual spectroscopic modeling of the other Alu components with multivariate calibration is a subject of another study which is currently under investigation. As a result, multivariate calibration models that are based on FTIR spectroscopy were generated with the 136 real samples mentioned above in the calibration and independent validation sets. As indicated before, half of these samples contained Nafol as additive and the rest had Cindolube. Therefore 68 of these samples were used to determine Nafol content and the other 68 of them were used to determine Cindolube content. On the other hand, the contaminants would be the same in both systems and therefore all of these 136 samples were used to model Alu 16 and total Alu contents.

In order to generate multivariate calibration models for Alu 16 and total Alu contents, the samples were numbered form 1 to 136 and all the odd numbered samples were taken as calibration set and the remaining even numbered samples were reserved as an independent validation set. For the additives Nafol and Cindolube, 68 samples were divided into two subsets as calibration and validation sets as described above for both components. As indicated before, GILS is based on an evolutionary iterative variable selection procedure and if an appropriate precaution is not undertaken it could possibly generate over fitted calibration models. Therefore it was set to operate with a leave one out cross validation algorithm in each iteration step. However in order to have a double check on the predictive ability of the models an independent validation set were also used at the end of the GILS algorithms. In all the calibration models described here, GILS were set to run with 30 genes and 100 iterations. Fig. 5 shows the reference vs. predicted plots of Nafol, Cindolube, Alu 16 and total Alu which contains Hydrotex Alu 46, Recompound Alu 100, 220, 320, and 460. The multivariate calibration models that are based on FTIR spectra of process samples had good predictive ability for the independent validation samples. The R^2 values given on the plots are for the calibration set samples and they were all around 0.99 except for the Alu 16

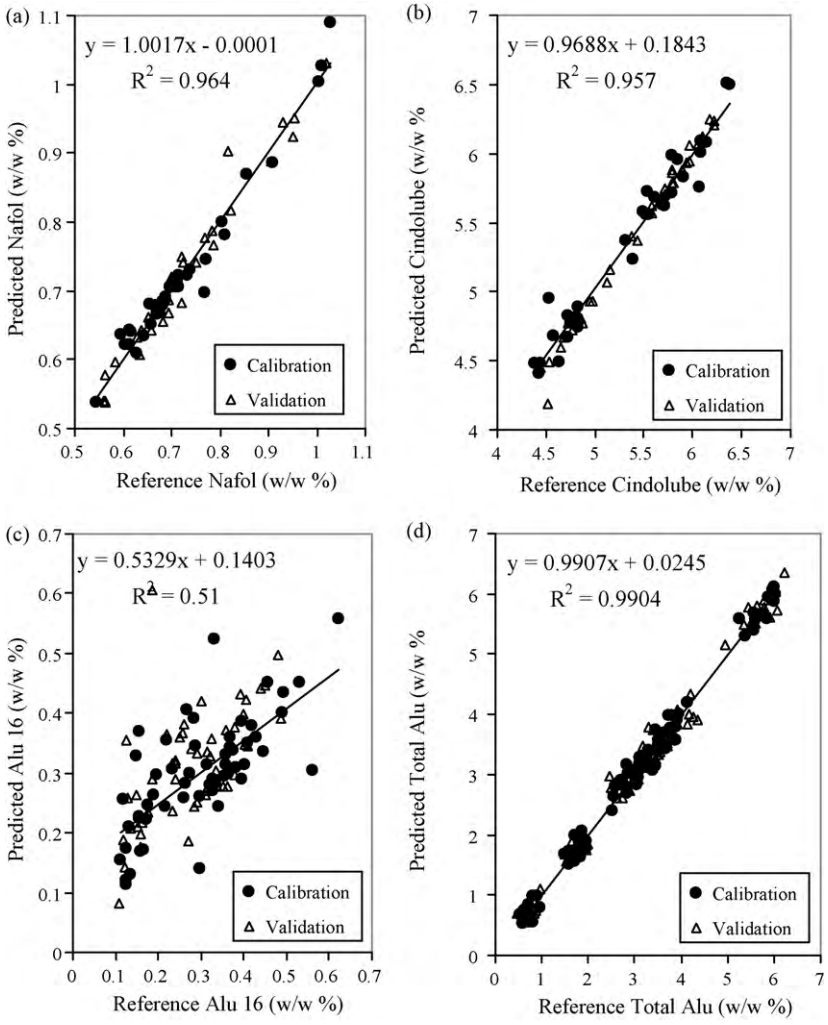

Fig. 6. Reference values obtained from GC analysis vs. PLS predictions based on FTIR spectra for the additives (a) Nafol and (b) Cindolube and for the contaminants (c) Alu 16 and (d) Total Alu contents.

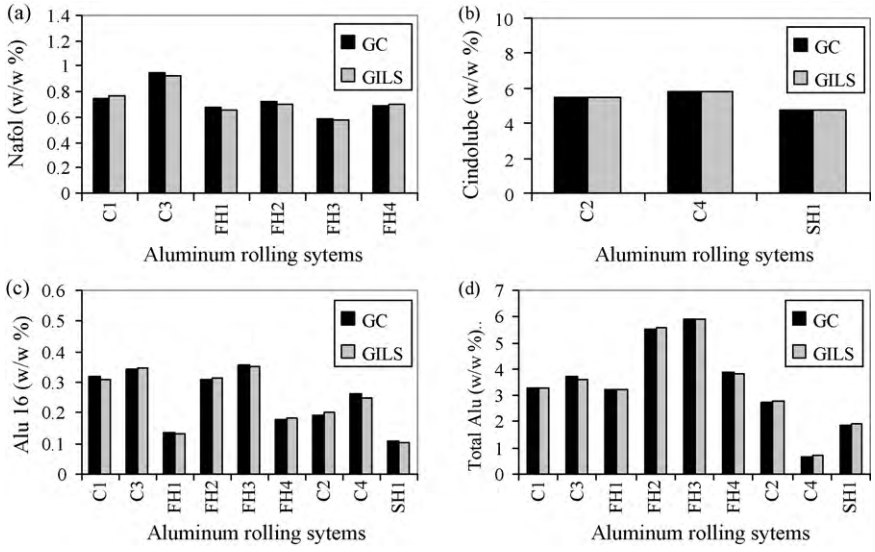

Fig. 7. Comparison of the GC vs. GILS predictions of the (a) Nafol, (b) Cindolube, (c) Alu 16, and (d) Total Alu contents in rolling oils taken from 9 different rolling systems.

Table 1
The SEPCV and SEP values along with the number of PLS factors selected from leave one out cross validation for the PLS and GILS models.

Method	SEPCV and SEP	Nafol	Cindolube	Alu 16	Total Alu
PLS	SEPCV (w/w%)	0.03	0.13	0.09	0.15
	SEP (w/w%)	0.07	0.07	0.09	0.18
	Number of PC	16	14	3	9
GILS	SEPCV (w/w%)	0.01	0.06	0.03	0.15
	SEP (w/w%)	0.03	0.06	0.04	0.18

which resulted in a R^2 value of 0.96. On the other hand, R^2 values for the independent test set would be more informative for the long term reliability of the models. However, the R^2 values for the independent test samples were slightly less than the values for Nafol additive and Alu 16. The values were 0.93 for Nafol, 0.87 for Alu 16, and 0.99 for both Cindolube and Total Alu. Among the models developed by GILS, Alu 16 results seem to deviate more from the GR reference values. This can be explained when the pure component spectrum of Alu 16 is compared with the other components studied. As seen from Fig. 4, Alu 16 gave weak peaks for a 1.0% (w/w) standard sample where as maximum Alu 16 concentrations for the most of the process samples analyzed with GC were around 0.5% by weight. As a result of these weak spectral features, relatively poor multivariate calibration model was generated for the contaminant Alu 16. Overall, the standard error of prediction from cross validation (SEPCV) and standard error of prediction (SEP) values were 0.025% and 0.037% by weight, respectively, for calibration and independent validation sets.

The fact that Cindolube and Nafol gave much stronger infrared absorption than the contaminants Alu series, very good multivariate calibration models were constructed for these two additives. However, the results of independent validation set for Nafol were not as good as that of Cindolube. This could be the result of much higher concentration of Cindolube in the process samples resulting in a much stronger infrared peak. In fact the concentration of Cindolube in the process samples was almost 10 times higher than the concentration of Nafol in the samples. The SEPCV and SEP values for Nafol were 0.012% and 0.034% by weight, respectively. On the other hand, both SEPCV and SEP values were the same (0.055%, w/w) for Cindolube indicating a very robust and strong model based on spectroscopic determination.

When the result of Total Alu content was examined in Fig. 5, it is seen that at least four different degrees of contamination takes place in the process samples. However, a single calibration model was sufficient to model in all these samples and the results for the independent validation set was almost as good as the results for the calibration set. The SEPCV and the SEP values were 0.15% and 0.18% by weight, respectively.

The GILS approach constructs multivariate calibration models based on a genetic algorithm through an iterative variable selection step, and we compared its prediction ability to that of PLS as the most commonly used multivariate calibration method. The same calibration and independent validation sets were used in order to directly compare the predictive performance of GILS and PLS. Fig. 6 shows the predicted vs. reference concentration plots for Nafol, Cindolube, Alu 16 and total Alu using the PLS calibration method. When compared with the GILS results in Fig. 5, the PLS calibration model generated for total Alu yielded results comparable to those of GILS with a R^2 value of 0.99. However, the PLS result for Alu 16 was poor with a R^2 value of 0.52 whereas the calibration model generated with GILS for Alu 16 gave a R^2 value of 0.96. In addition, PLS calibration models for Nafol and Cindolube gave R^2 values around 0.96 compared to R^2 values near 0.99 based upon the GILS models for the same components. The SEPCV and SEP values along with the number of PLS factors selected from leave one out cross validation

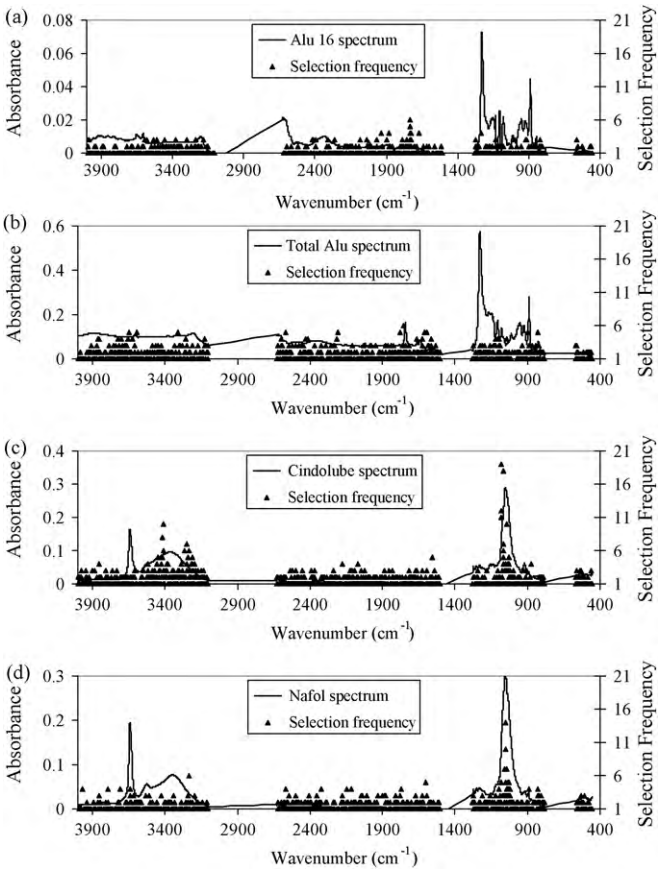

Fig. 8. Distribution of selected wavenumbers along with corresponding pure component spectrum (a) Alu 16, (b) Total Alu, (c) Cindolube, and (d) Nafol.

are given in Table 1 for both the PLS and GILS models. Selection of optimum number of PLS factors was done with prediction error sum of squares (PRESS) from leave one out cross validation. Note that GILS is not a factor based calibration method. As seen in Table 1, calibration models built with PLS required relatively large number of PLS factors for Nafol and Cindolube whereas model for total Alu required 9 PLS factors. The poor results obtained with PLS for Alu 16 may be a result of the fact that the optimal number of PLS factors used to construct the model is only 3 for this analyte. When more PLS factors were used to generate calibration models for Alu 16, the SEPCV was dramatically increased suggesting that PLS was unable build a robust calibration model.

In order to illustrate the contents of the additives and the contaminants in each particular process samples investigated in this study, a bar graph is given in Fig. 7 which compares GC result with GILS results. The fact that there were a large number of samples from each rolling system, only average determinations was illustrated in this plot for each system. As seen from the figure, the highest total Alu contamination is seen in FH2 (5.50%, w/w) and FH3 (5.90%, w/w) whereas lowest contamination is observed in C4 (0.68%, w/w) system. For Alu 16 determination, FH1 and SH1 systems had lowest percent contamination which was around 0.10% by weight where as C3 and FH3 had about 0.36% Alu 16 contaminations. The Nafol and Cindolube contents of the rolling systems indicate that there is a good agreement between GC and GILS determinations.

The fact that the GILS relies heavily on the random processes, it was also set to run 50 times for each component in order to determine selection frequencies of the most used wavenumbers (wavelengths) in the multivariate calibration steps. Fig. 8 shows the selection frequencies of the selected wavenumbers along with

the pure component spectrum of Alu 16, Nafol, Cindolube and a mixture of total Alu components that are modeled in this study. As seen from Fig. 8, selection frequencies for Nafol and Cindolube were localized mainly in the regions where most dominating peaks are observed for these components. On the other hand, the highest selection frequencies for Alu 16 and total Alu components are away from the regions where peaks for Nafol and Cindolube overlaps especially around 1200 cm^{-1} even though the Alu components had rather more intense and broader peaks around 1200 cm^{-1}. In fact, the most frequently selected wavenumbers for Alu components were seen between 1600 and 1700 cm^{-1} region where weak peaks are seen for these components. These results showed that the GILS method was very effective to extract necessary information while constructing multivariate calibration models resulting in a robust component specific modeling despite all the overlapping features in the spectra.

4. Conclusion

Results had shown that the GILS method is able to model rolling oil additives and contaminant concentrations successfully using FTIR spectra of the process samples. Multivariate calibration models that are generated with GILS was component specific as observed from selection frequency plots indicating that with all the overlapping and complex nature of the FTIR spectra of the multicomponent mixtures, the GILS algorithm only focuses on the regions where the most concentration related information is contained. Comparison of GILS models with PLS models revealed that the same prediction performance was observed for total Alu whereas GILS generated relatively better calibration models for other components studied. Determination of the contaminants based on FTIR spectroscopy coupled with multivariate calibration offers a much faster analysis that could allow continuous monitoring of the production process.

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