

# Supercritical fluid extraction followed by gas chromatography-mass spectrometry determination of electrical-grade insulating oil residues from activated bauxite

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## Abstract

The electrical-grade insulating oils widely used in high-voltage power equipment produce degradation by-products during their service life. Filtering the aged oil through an adsorbent material such as activated bauxite usually eliminates such by-products. As a consequence the adsorbent will be contaminated with several chemical species thus hindering its direct discharge in the environment. In the present work, a methodology was developed and optimized to extract oil residues adsorbed in activated bauxite by dynamic supercritical fluid extraction (DYN-SFE) employing CO<sub>2</sub> as extraction solvent. Characterizing the extracted residues by GC-MS allowed following the remediation process, showing that the developed method was effective in extracting the vast majority of the compounds detected in the insulating oil studied. However, the extraction of carboxylic acids from oil degradation requires to be optimized in a future study.

**Keywords:** SFE; GC-MS; insulating oil; activated bauxite; remediation; CO<sub>2</sub>.

## 1. Introduction

Electrical-grade insulating oils have been widely used as an insulating fluid and a heat exchange medium since 1890. Such an application is concentrated in the most apparatuses installed on electric power transmission and distribution systems. In order to perform its task, insulating oils must maintain the dielectric strength and the heat dissipation characteristics when used in power transformers<sup>[1]</sup>.

The insulating oil is frequently called mineral oil to differentiate it from vegetable and animal oils since it is manufactured from crude petroleum, which is geologically classified as a rock. The crude oil is distilled and separated in distinctly different commercial fractions from which several industrial products are obtained. The fraction separated in distillation towers at temperatures between 300-400°C is employed in the production of insulating oils<sup>[2]</sup>.

An insulating oil is composed basically by aliphatic, cycloaliphatic and mono-, di-, tri- and polycyclic aromatic hydrocarbons. A minimum amount of compounds containing sulphur, nitrogen and oxygen atoms can also be found.

Oil molecules oxidize in the presence of oxygen and metallic catalysts when heated at a high temperature (e.g. 100°C)<sup>[3]</sup>. A series of reactions occurs in the presence of oxygen, and the following oxidation products are formed: alcohols (ROH), aldehydes (RCHO), ketones (RCOR), carboxylic acids (RCOOH), esters (RCOOR), etc.

A process called reclamation performs the reduction in the amount of acidic contaminants and of other oil oxidation by-products. Typically the oil is percolated through a bed of an adsorbent material. In Brazil, one of the world's leading bauxite producers<sup>[4]</sup>, this mineral is activated at 600°C being the most widely used adsorbent material to perform such a task.

Bauxite is a naturally occurring type of clay with a relatively high surface activity<sup>[5]</sup>. It is obtained

from deposits that supply raw material to aluminum manufacturing plants. Bauxite surface presents aluminum and oxygen atoms, as well as hydroxyl groups (-OH). The selective adsorption of polar molecules depends mainly on hydrogen bonds with Al-OH sites. Therefore, bauxite efficiency in the removal of oxidation compounds is in accord with the following order:

hydroperoxides > acids > alcohols > ketones > hydrocarbons (aromatic and aliphatic)

Insulating oil reclamation provides both technical and economic benefits to electric power utility companies, but the final disposal of used bauxite causes legal and environmental concerns. Around 5% of the mass of oil before reclamation remain adsorbed in the bauxite and turn it into an environmental pollutant. The disposal of bauxite contaminated with insulating oil residues has become very expensive lately due to restrictions imposed by the environmental protection agency of the State of Sao Paulo, Brazil<sup>[6-9]</sup>.

The present study was conducted to develop a method to extract insulating oil residues from activated bauxite by supercritical CO<sub>2</sub>, thus isolating the contaminants from bauxite and allowing its re-utilization. The method efficiency was tested in a sample of oil that had been previously oxidized in power transformers in service.

## 2. Experimental

### 2.1. Samples

An oil sample was collected from a power transformer in service on the system of the power distribution utility Companhia Paulista de Força e Luz (CPFL), Brazil. This oil (type AV-58) was manufactured by Petrobras, a Brazilian oil refiner. The percolation of the oil sample was performed through a bed of unused and decontaminated activated bauxite (20-60 mesh) supplied by Mineracao Curimbaba, Brazil.

## 2.2. Gravimetric study of the extraction of spiked samples with Supercritical CO<sub>2</sub>

This part of the study was planned to evaluate the influence of basic parameters such as supercritical temperature and pressure, flow rate, restrictor system, sample collection system, and others on the extraction of typical compounds frequently found to adsorb in bauxite employed for insulating oils reclamation.

A dynamic extraction system employing a supercritical fluid, developed at the Chromatography Laboratory of the Institute of Chemistry of Sao Carlos (IQSC), University of Sao Paulo, was utilized. A preliminary extraction of the bauxite *in natura* was conducted with CO<sub>2</sub> at 200 atm and 60 °C to eliminate contaminants. The process was repeated three times, and a total volume of 750 mL of CO<sub>2</sub> was pumped through the sample since the pump flow volume is 250 mL.

The main compounds present in the oil were already identified by high resolution gas chromatography coupled to mass spectrometry (GC-MS) in a previous study<sup>[10]</sup>. Based on the results obtained, some spiked compounds were selected to represent the most important compound classes present in the oil. Samples of unused and decontaminated bauxite weighing 5.0 g were prepared. Each of them was spiked with 50 mg of one of the following compounds: n-nonadecane, naphthalene, or methyl myristate ester. These compounds were adsorbed by the bauxite samples. The extraction was conducted with supercritical CO<sub>2</sub> under the following experimental condition:

- Pressure: 150, 200 and 250 atm;
- Temperature: 50, 60 and 70 °C;
- Restrictor: stainless steel tube with 100 and 250 µm i.d.;
- Extraction duration: 2 min;
- Restrictor length: 50 cm.
- The extracts were collected in test tubes, and the samples were weighed.

## 2.3. Oil residue extraction with Supercritical CO<sub>2</sub>

A sample weighing 15.0 g of unused and decontaminated bauxite was placed in a glass funnel with a cotton tuft at the bottom. The bauxite was saturated with 300 mL of oxidized insulating oil which was slowly filtered by gravity for 24 hours. The eluted oil was disposed of.

The bauxite sample was divided into three aliquots of 5.0 g each. Three extractions with the dynamic extraction system developed were carried out in accordance with the parameters previously established during the optimization of the experimental conditions for the spiked compounds:

- Temperature: 60 °C;
- Restrictor: stainless steel tube with 250 µm i.d.;
- Extraction time: 2 min;
- Restrictor length: 50 cm.

The extraction pressure was the only parameter changed during this step, being utilized 150, 200 and 250 atm. These three experiments provided three oil extracts, whose chemical composition was further evaluated.

## 2.4. Fractionation by Preparative Liquid Chromatography (PLC-8)

An original oil sample, which was taken as a reference, and the three oil extracts were fractionated by preparative liquid chromatography using the method PLC-8<sup>[11]</sup>. Each sample weighing 300 mg was placed at the top of a preparative chromatography glass column (50 cm × 11 mm), containing 20 g of silica gel 60 (E.M. Merck, 7734), 70-230 mesh, used as a stationary phase. The silica gel was activated in the oven at 140 °C for 4 hours. The fractions were eluted by an adequate solvent sequence. The elution characteristics and the fractions obtained are presented in Table 1. The increase in solvent polarity produces five hydrocarbon fractions (F-1 through F-5), one intermediate resin fraction (F-6) and two heavy fractions called Asphaltenes (F-7) e asphaltols (F-8).

**Table 1.** Elution condition employed in the Preparative Liquid Chromatography fractionation (PLC-8).

	Eluent	Elution vol. (mL)	Chemical class
F-1	Hexane (C-6)	40	Saturates
F-2	Hexane (C-6)	27	Monocyclic Aromatics
F-3	11,5% Bz in C-6	36	Dicyclic Aromatics
F-4	32% Bz in C-6	24	Tricyclic Aromatics
F5	32% Bz in C-6	25	Polycyclic Aromatics
F-6	Bz: Ac: MeCl <sub>2</sub> (3:4:3)	65	Resins
F-7	Ac: THF (2:8)	60	Asphaltenes
F-8	Methanol	65	Asphaltols

Bz - Benzene MeCl<sub>2</sub> - Dichloromethane Ac - Acetone THF - Tetra-hydro-furan.

### 2.5. High Resolution Gas Chromatography coupled to Mass Spectrometry (HRGC-MS)

The volatile fractions (F-1 to F-6) of the reference oil and of the three oil extracts were analyzed by HRGC-MS. A Hewlett-Packard gas chromatograph, model 5890 A, fitted with a selective mass detector (MSD), model HP5890, operating in the electron impact mode with 70 eV of ionization energy was used. An in-house fused silica capillary column (50 m × 0.25 mm × 0.7 μm) coated with a film consisting of 5% of phenyl-methylsiloxane / 95% dimethylpolysiloxane was used. The following chromatographic condition were utilized:

- Flow gas : helium (35 cm/s);
- Split ratio: 1:20;
- Injected volume: 1 μL;
- Scan velocity: 1 scan/s;
- Scan interval: 50 – 475 u.m.a.;
- Injector temperature: 250°C;
- Interface temperature: 300°C;
- Oven temperature programming: 80°C (1min) - 4°C/min - 300°C (30min).

F-1 fractions were diluted in 1 mL of hexane for analysis. The other fractions were diluted in 1 mL of dichloromethane. Data process was performed in a CPU, model HP7946. The database used was NBS-REVE.

## 3. Results and discussion

### 3.1. Fractionation of the samples extracted by CO<sub>2</sub> employing Preparative Liquid Chromatography (PLC-8)

Table 2 shows the results of the fractionation of the oil samples by the PLC-8 method. The oil extract samples had the relative distribution of most of their fractions changed as compared to that of the reference oil. These results can be at least partly attributed to the fact that bauxite adsorbs the more polar compounds preferentially as compared to hydrocarbons. Saturated hydrocarbons tend to be less retained by bauxite as compared to aromatics since the later fraction contains compounds that are polarizable. The percentages of saturated hydrocarbons (F-1) of the extracted oils were always lower than that of the reference oil. The sum of the relative percentages of the aromatic hydrocarbons (F-2 to F-5) was 16% for the reference oil and 23.4%, 27% and 20.5% for the oil extracts obtained at 150, 200 and 250 atm, respectively. The percentage of resins (F-6) of the oil extracts increased significantly to 7.5% while that of the reference oil was 4.2%. The analyses of the oils by HRGC-MS revealed that there was a high concentration of dicyclic aromatics in fractions F-6 of the oil extracts. Fractions F-7 and F-8 presented a minimum variation.

**Table 2.** Relative distribution (%) of the products obtained from fractionation of the oils by PLC-8.

Fraction	Reference oil	Oil extract at		
		150 atm	200 atm	250 atm
F-1	78.7	68.0	64.3	70.7
F-2	12.0	18.5	21.2	13.7
F-3	1.6	2.0	3.3	2.8
F-4	1.4	1.7	1.7	3.0
F-5	1.0	1.2	0.8	1.0
F-6	4.2	7.5	7.5	7.5
F-7	0.6	0.7	0.7	0.8
F-8	0.5	0.4	0.5	0.5

### 3.2. Gravimetric study of Supercritical CO<sub>2</sub> extraction of spiked samples

The results from the extraction of spiked samples are presented in Tables 3 to 5. As the data show, the best extraction results for the three spiked samples studied were obtained at 200 atm of pressure, and at temperatures of 60 and 70°C, with the restrictor with 250 µm of internal diameter. Under such a condition, extraction was 97% in mass for methyl myristate, and 98% for both naphthalene and n-nonadecane.

The extraction at 150 atm (Table 3) had the worst performance since the percentage of spiked extractions reached a maximum of 50% in mass. The extraction at 250 atm (Table 5) presented better results than those

**Table 3.** Influence of the temperature and restrictor diameter on the extraction of spiked oil employing CO<sub>2</sub> at 150 atm as the extraction solvent.

Temperature (°C)	Restrictor diameter (µm)	Extraction percentage (%)		
		1	2	3
50	100	12	-	25
60	100	12	-	28
70	100	12	-	25
50	250	35	10	35
60	250	48	10	50
70	250	48	10	50

1 - n-nonadecane; 2 - naphthalene; 3 - methyl myristate.

**Table 4.** Influence of the temperature and restrictor diameter on the extraction of spiked oil employing CO<sub>2</sub> at 200 atm as the extraction solvent.

Temperature (°C)	Restrictor diameter (µm)	Extraction percentage (%)		
		1	2	3
50	100	75	80	75
60	100	88	90	91
70	100	86	93	93
50	250	97	96	-
60	250	98	98	97
70	250	98	98	97

1 - n-nonadecane; 2 - naphthalene; 3 - methyl myristate.

obtained at the extraction at 150 atm, and reached up to 85% in mass. However, these results were poorer than those of the extraction at 200 atm (Table 4).

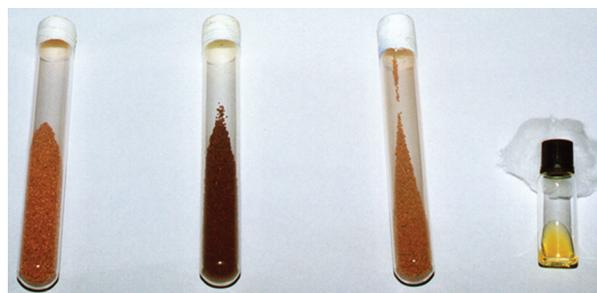
**Table 5.** Influence of the temperature and restrictor diameter on the extraction of spiked oil employing CO<sub>2</sub> at 250 atm as the extraction solvent.

Temperature (°C)	Restrictor diameter (µm)	Extraction percentage (%)		
		1	2	3
50	100	70	70	70
60	100	85	85	88
70	100	85	85	85
50	250	75	78	75
60	250	76	75	75
70	250	77	78	75

1 - n-nonadecane; 2 - naphthalene; 3 - methyl myristate.

### 3.3. High Resolution Gas Chromatography coupled with Mass Spectrometry (HRGC-MS) profile of oil samples extracted by Supercritical CO<sub>2</sub>

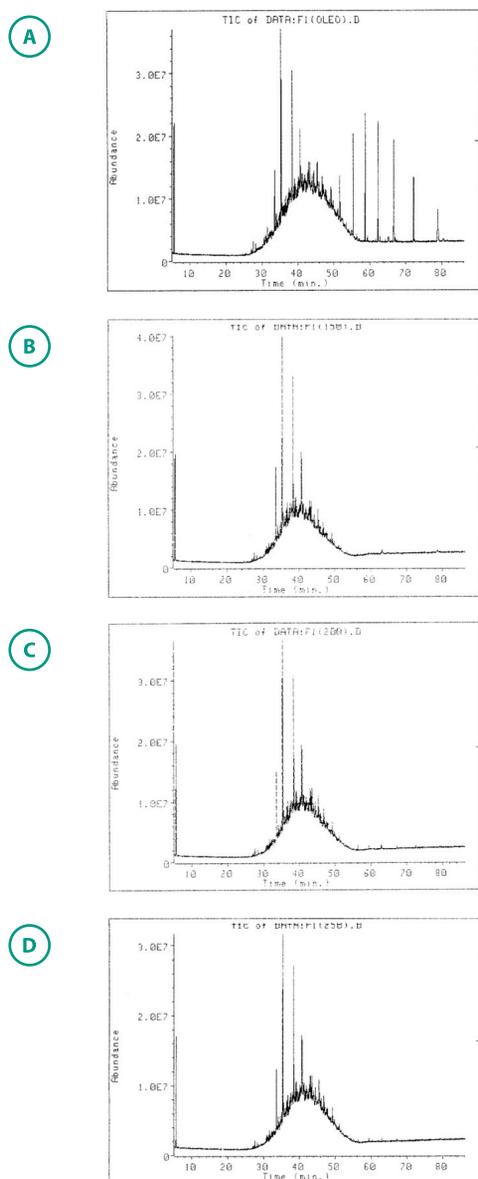
It was possible to visually confirm that the extraction process of real oil samples presented satisfactory results. Figure 1 shows test tubes containing samples of new bauxite before use, bauxite with oil residues before and after extraction, as well as a glass container with oil residue extracted at 200 atm. The visual aspect of the bauxite after extraction is very close to that of the new one which was used as a blank.



**Figure 1.** Test tubes containing: (a) samples of new bauxite before use; (b) contaminated bauxite containing oil residues before extraction; (c) bauxite after extraction; (d) a glass container with oil residue extracted at 200 atm.

Figure 2 show the chromatograms of fraction F-1 of the clean oil used as a reference and of the oil samples obtained from the same oil after extraction with supercritical CO<sub>2</sub> at 150, 200, and 250 atm of pressure, respectively.

The compounds whose peaks are shown in Figure 2 after 50 minutes of elution time correspond to a homologous series of long-chain carboxylic acids. The



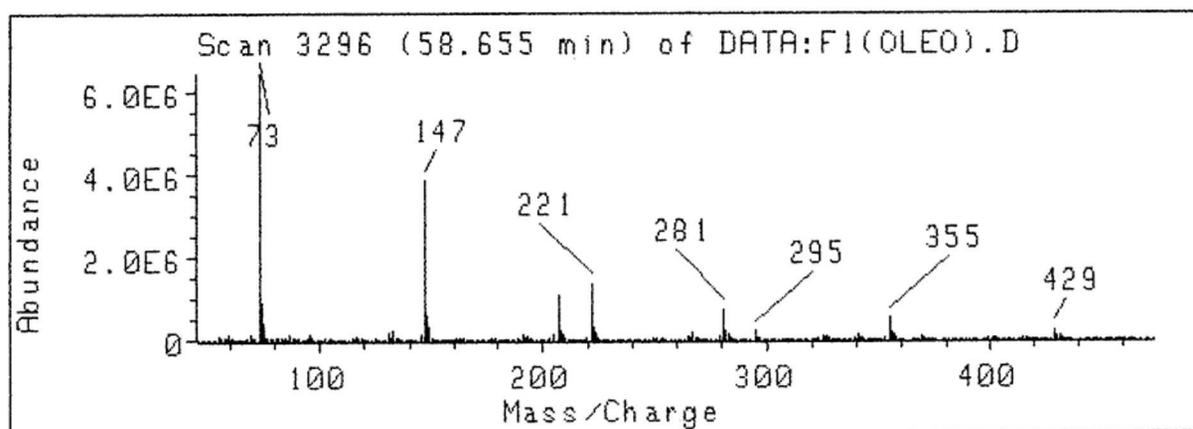
**Figure 2.** TIC of fractions F-1. (a) reference oil; (b) oil extract obtained by DYN-SFE at 150 atm; (c) oil extract obtained by DYN-SFE at 200 atm; (d) oil extract obtained by DYN-SFE at 250 atm.

carboxylic acids were expected to elute mostly at resin fraction (F-6). However, they were detected in all of the previous fractions from F-1 through F-5 of the reference oil (figures 4a, 5a, and 6a). Because of the high molecular weight of such acids, which is evidenced by their long retention time, we noticed a poor elution selectivity of the more polar solvents used in the fractionation by the PLC-8 method. The long hydrocarbon chain bonded to the acid radicals also has a good affinity for the less polar solvents and for hexane. Figure 3 shows the fragmentogram of a typical long-chain carboxylic acid detected in fraction F-1 of the reference oil.

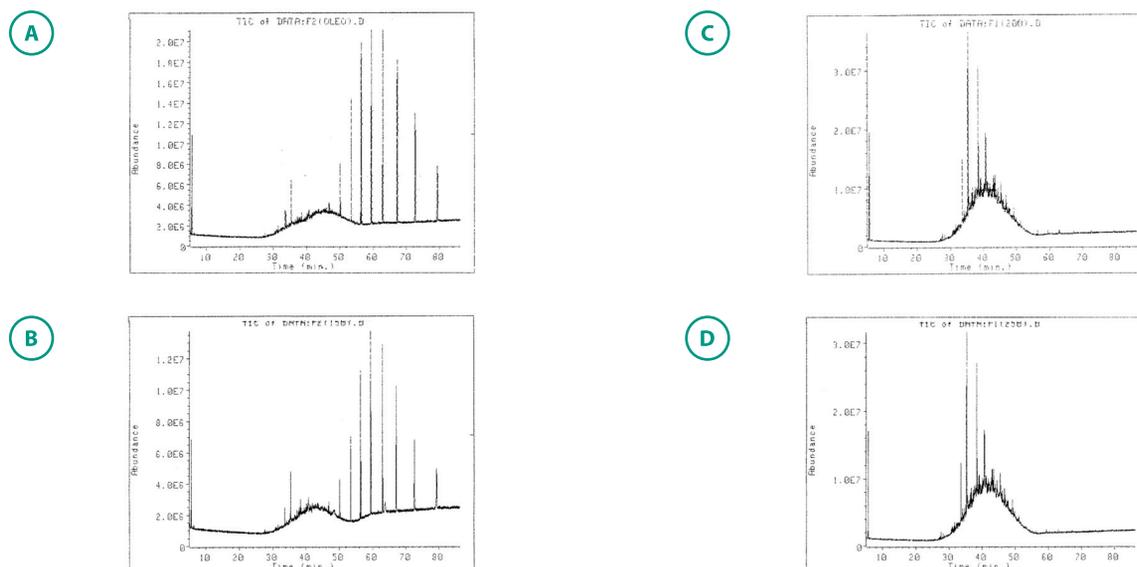
A satisfactory extraction of linear and branched long-chain alkanes detected up to a retention time of approximately 50 minutes was obtained. The carboxylic acids that eluted thereafter were extracted at very low concentration and only at the pressure of 200 atm.

The monocyclic aromatic hydrocarbon fractions (F-2) of the four samples analyzed presented few compounds detected within a retention time up to 50 minutes (Figure 4). However, a significant concentration of carboxylic acids was detected thereafter in the reference oil sample (Figure 4a). The compounds eluting at a retention time before 50 minutes were successfully extracted at the three pressures used. A significant extraction of the carboxylic acids was obtained only in the extraction performed at 200 atm. No detectable extraction of these acids was observed at the other extractions.

The di-, tri- and polycyclic aromatic hydrocarbon fractions (F-3 and F-4) analyzed also presented very few compounds detected within a retention time up to 50 minutes. Figure 5 show the chromatograms of fractions F-3, F-4 and F-5 of the reference oil, respectively. The chromatograms obtained from the extractions of all of these three fractions were extremely poor for the oil extracts obtained at 150, 200, and 250 atm. No significant extraction of any class of compounds was observed in such cases.



**Figure 3.** Fragmentogram of a long-chain carboxylic acid (retention time at 58,655 min), detected in the saturated hydrocarbon fraction of the reference oil.

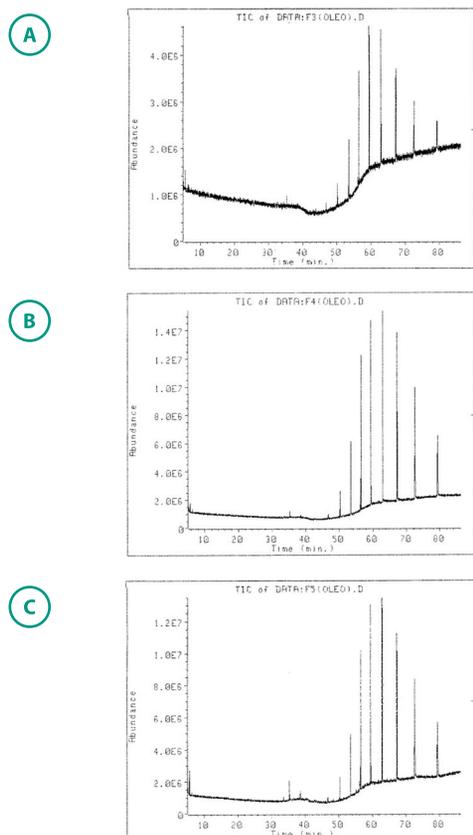


**Figure 4.** TIC of fractions F-2. (a) reference oil; (b) oil extract obtained by DYN-SFE at 150 atm; (c) oil extract obtained by DYN-SFE at 200 atm; (d) oil extract obtained by DYN-SFE at 250 atm.

The resin fraction (F-6) of the reference oil presented a low concentration of compounds up to a retention time of approximately 46 minutes (Figure 6a). However, thereafter a significant concentration of carboxylic acids was comparatively detected once again.

Several compounds were extracted in the experiments conducted with the contaminated bauxite at the three pressures employed. Taking into consideration the data of the extraction performed at 250 atm (Fig. 6d), it is possible to conclude that the more intense peaks

refer to long linear chain alkanes with retention times varying from 33 – 39 minutes; athracenone isomers, with retention times of 39.623, 40.630 and 41.018 minutes; and aromatic compounds bonded to alkyl groups with a retention time range from 41 – 48 minutes. The majority of the compounds with retention times before 50 minutes were successfully extracted in the three extractions performed. However, the extraction of the carboxylic acids has to be further investigated in order to better understand its behavior.

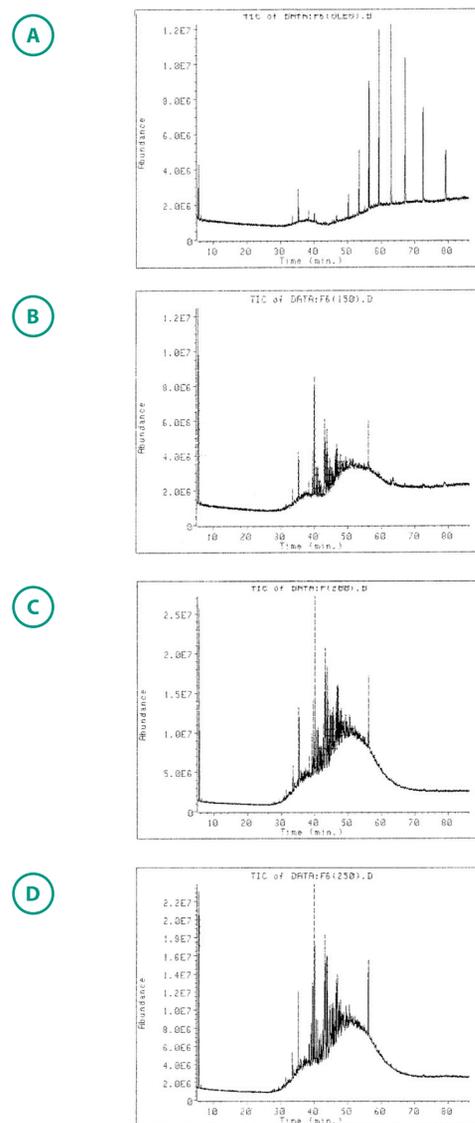


**Figure 5.** TIC of fractions from the reference oil; (a) F-3; (b) F-4; (c) F-5.

#### 4. Conclusion

The main components of the several classes of chemical compounds of an electrical-grade insulating oil sample were determined by preparative liquid chromatography fractionation employing the method PLC-8 and by high resolution gas chromatography coupled with mass spectrometry (HRGC-MS).

The method developed to extract by supercritical carbon dioxide the residues of insulating oil adsorbed in activated bauxite was effective to extract spiked compounds in a preliminary study. The described method was also effective in extracting the majority of the compounds detected in the insulating



**Figure 6.** TIC of fractions F-6. (a) reference oil; (b) oil extract obtained by DYN-SFE at 150 atm; (c) oil extract obtained by DYN-SFE at 200 atm; (d) oil extract obtained by DYN-SFE at 250 atm.

oil studied. However, the extraction of carboxylic acids from oil oxidation requires to be optimized in a future study. Modifiers such as methanol and ethanol, among others are being investigated aiming to improve the extraction efficiency of this particular class of contaminants.

## References

1. CLARK, F.M. *Insulating materials for design and engineering practice*. New York, John Wiley and Sons Inc., 1962. 1217 p.
2. LIPSHTEIN, R.A.; SHAKNOVICH, M.I. *Transformer oil*. Jerusalem, Wiener Bindery, 1970. 257 p.
3. LAMARRE, C. *Resistance to oxidation of reclaimed transformer oils*. Montreal, Canadian Electrical Association, 1986. 44 p.
4. PRADO, C.M.R.; ALVES, M.I.R.; LELES, M.I.G.; MEDEIROS, R.I.; OTTO, C.R.N.; DAMASCENO, F.C.; BRAIT, C.H.H.; FRANCO, P.I.B.M.M ANTONIOSI FILHO, N.R., *Study of acid activation and thermal treatment of bauxite extracted from deposits in Minas Gerais, Brasil*. *Ceramica* 58, 111-117, 2012.
5. PILUSKI, J.E.A.; HOTZA, D. *Characterization of activated bauxite before and after saturation with insulating mineral oil*. *Quim. Nova* 31(5) 1165-1169, 2008.
6. Associação Brasileira de Normas Técnicas; NBR 10004: Resíduos Sólidos – Classificação, 2004.
7. Associação Brasileira de Normas Técnicas; NBR 10005: Procedimento para Obtenção de Extrato Lixiviado de Resíduos Sólidos, 2004.
8. Associação Brasileira de Normas Técnicas; NBR 10006: Procedimento para Obtenção de Extrato Solubilizado de Resíduos Sólidos, 2004.
9. Associação Brasileira de Normas Técnicas; NBR 10007: Amostragem de Resíduos Sólidos, 2004.
10. BASSETTO F., A. *Chemical study of electrical-grade insulating oil through chromatographic techniques, mass spectrometry, supercritical fluid extraction and radiolytic degradation*. Sao Carlos, SP, Brasil, 1998. 231 p. Ph.D. Thesis, Institute of Chemistry of Sao Carlos, University of Sao Paulo, Brasil (in Portuguese).
11. KARAM, H.S.; McNAIR, H.M.; LANÇAS, F.M. *LC-GC*, v.5, n.1, p.41, 1987.