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BIBLIOMETRIC ANALYSIS AND RESEARCH TRENDS ON CHLORIDE DETERMINATION IN THE OIL INDUSTRY

ANÁLISE BIBLIOMÉTRICA E TENDÊNCIAS DA PESQUISA SOBRE DETERMINAÇÃO DE CLORETOS NA INDÚSTRIA DO PETRÓLEO

ANÁLISIS BIBLIOMÉTRICO Y TENDENCIAS DE INVESTIGACIÓN SOBRE LA DETERMINACIÓN EN LA INDUSTRIA PETROLERA

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ABSTRACT

The presence of inorganic chlorides, even at low concentrations in petroleum, is associated with a series of operational problems. The determination of inorganic chlorides plays an important role in the petroleum industry. In this study, a bibliometric analysis using the free VOSviewer application and the Web of Science database was performed to provide an overview on the application of chloride determination in petroleum. A total of 3117 articles were analyzed on various aspects of publication characteristics such as publication production, countries, institutions, journals, highly cited articles and keywords. The number of publications in this application has steadily increased over the past 23 years. China and USA were the countries with the highest link strength index. China played a central role in the network of collaboration between the most productive countries. The Federal University of Santa Maria (UFSM) was the institution with the highest link strength (88). Energy & Fuels was the most productive newspaper (173). The keywords surface tension, ionic liquids, emulsion, demulsification, adsorption, zeta potential and wettability are considered critical future research points.

RESUMO

A presença de cloretos inorgânicos, mesmo em baixas concentrações no petróleo, estão associados a uma série de problemas operacionais. A determinação de cloretos inorgânicos tem importante papel na indústria do petróleo. Neste estudo, uma análise bibliométrica usando o aplicativo gratuito VOSviewer e a base de dados da Web of Science foi realizada para fornecer uma visão geral na aplicação da determinação de cloretos em petróleo. Um total de 3117 artigos foram analisados em vários aspectos das características da publicação, como produção de publicações, países, instituições, periódicos, artigos altamente citados e palavras-chave. O número de publicações nesta aplicação aumentou de forma constante nos últimos 23 anos. China e EUA foram os países com maior índice de link strength. A China teve um papel central na rede de colaboração entre os países mais produtivos. A Universidade Federal de Santa Maria (UFSM) foi a instituição com maior link strength (88). Energy & Fuels foi o jornal mais produtivo (173). As palavras-chave tensão superficial, líquidos iônicos, emulsão, desemulsificação, adsorção, potencial zeta e molhabilidade são considerados futuros pontos críticos de pesquisa.

RESUMEN

La presencia de cloruros inorgánicos, incluso en bajas concentraciones en el petróleo, está asociada a una serie de problemas operativos. La determinación de cloruros inorgánicos juega un papel importante en la industria del petróleo. En este estudio se realizó un análisis bibliométrico utilizando la aplicación gratuita VOSviewer y la base de datos Web of Science para brindar una visión general en el campo de la determinación de cloruros en el petróleo. Se analizaron un total de 3117 artículos sobre diversos aspectos de las características de las publicaciones, como producción de publicaciones, países, instituciones, revistas, artículos muy citados y palabras clave. El número de publicaciones en este campo ha aumentado constantemente durante los últimos 23 años. China y EUA fueron los países con mayor nivel de link strength. China jugó un papel central en la red de colaboración entre los países más productivos. La Universidad Federal de Santa María (UFSM) fue la institución con mayor link strength (88). Energy & Fuels fue el periódico más productivo (173). Las palabras clave tensión superficial, líquidos iónicos, emulsión, demulsificación, adsorción, potencial zeta y humectabilidad se consideran puntos críticos de investigación futura.

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1 INTRODUCTION

The oil produced in the world has a unique chemical constitution, which varies according to the form of its geological formation - oil field - and some are obtained by mixing two or more fields (Stratiev et al., 2023; Coutinho et al., 2022 ; Shishkova et al., 2022; Speight, 2014). In Brazil, in 2022, approximately 75.3% of oil production came from the pre-salt layer, 19.4% from the post-salt layer and 5.3% from land (Agência Nacional de Petróleo [ANP], 2022). Brazilian oils extracted from offshore platforms have a high concentration of salts (Aguiar et al., 2022; Soares et al., 2022).

Petroleum can normally have two types of chlorides: inorganic chlorides and organic chlorides (Enders et al., 2020; Wu et al., 2018). Sodium chloride (NaCl), magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) are mainly responsible for inorganic chloride contamination in oil (Mitra et al., 2022). In Brazilian oils, this proportion of inorganic chlorides can vary: NaCl: 70–76%, $MgCl_2$: 7–20%, $CaCl_2$: 10-14% (Fernandes et al., 2022). Inorganic chlorides, mainly NaCl, $CaCl_2$ and $MgCl_2$, even at low concentrations in petroleum, are associated with a series of operational problems (Mitra et al., 2022; Pagliano et al., 2021; Wu et al., 2018). In the refinery, due to the thermal decomposition of chloride salts, the formation of hydrochloric acid may occur and consequently form corrosion in pipes, valves and pumps. Furthermore, saline deposits can adhere to catalysts, reducing efficiency and increasing energy consumption (Mitra et al., 2022).

To mitigate the problems caused by the presence of salt, oils are subjected to a desalination process (Mitra et al., 2022). This procedure is matrix dependent and its effectiveness is reduced when heavy oil fractions are processed (Gray et al., 2008). Process control is required to quantify residual chloride. However, the quantification of chlorides in oil samples is an analytical challenge.

The development of methods for determination of total chloride in oil and derivatives has been conducted using various analytical techniques: Neutron Activation (NAA) analysis (Katona et al., 2021; Adeyemo et al., 2006), X-Ray Fluorescence (XRF) (Doyle et al., 2011), digital imaging using colorimetry (Holkem et al., 2021), gas chromatography coupled to mass spectrometry (Gajdosechova et al., 2021), ion chromatography (Campos et al., 2020; Robaina et al., 2016), flame atomic absorption spectrometry (FAAS) (Silva et al., 2023), graphite furnace atomic absorption spectrometry (GFAAS) (Seeger et al., 2019), inductively coupled plasma optical emission spectrometry (ICP-OES) (Gazulla et al., 2022; Souza et al., 2015), inductively coupled plasma mass spectrometry (ICP-MS) (Nelson & Lopez-linares, 2019).

ASTM D512 (American Society for Testing and Materials, 2023) titrimetric method in water, ASTM D6470 (American Society for Testing and Materials, 2020) potentiometric and ASTM D3230 (American Society for Materials, 2020) electrometric methods. Testing and Materials, 2019) in oil. The determination of chlorides by the ASTM D6470 method has a number of disadvantages such as analysis time, projection and sample loss (Holkem et al., 2021; Campos et al., 2020). The ASTM D3230 method requires the construction of a calibration curve that relates conductivity to salt concentration (American Society for Testing and Materials, 2019) .

As these salt proportions vary greatly in the oil field, it makes the implementation of the methodology extremely laborious (American Society for Testing and Materials, 2019).

Sample preparation is a fundamental step for elemental analysis, as it ensures maximum detection of the analyte and eliminates interferences (Mello et al., 2012). Different sample preparation methodologies have been used in petroleum samples such as wet digestion, combustion, organic solvent dilution, emulsification, extraction and microextraction (Suliman et al., 2021; Gab-Allah et al., 2020; Mello et al., 2012). Analytical technologies such as microwave-assisted wet digestion, microwave-assisted extraction, ultrasound-assisted extraction, microwave-induced combustion, alkaline treatment and liquid-liquid extraction and other alternative approaches for inorganic elements are described in the literature (Santana et al., 2022).

Bibliometrics is a useful tool for qualitative and quantitative statistical analysis to describe patterns of distribution of articles within a given topic, providing a structured analysis for a large volume of information, helping to infer trends over time and identify changes in focus (Fu et al., 2013). The literature describes numerous tools and software that help collect and analyze data for bibliometric research (Aria & Cuccurullo, 2017; Synnestvedt et al., 2005). In addition to various free and open source software*,* it is possible to quickly view world productions in the Web of Science, Scopus, Dimension, Pubmed*,* databases*,* among others. The objective of this article is to evaluate publications on the determination of chlorides in petroleum through a longitudinal bibliometric analysis, applying statistical and mathematical methods to analyze trends, perspectives and hot topics in this research area.

2 METHODOLOGY

Web of Science database was chosen for its multidisciplinarity, large number of indexed journals, ease of access and cited reference search. The results presented in this article are based on a bibliometric analysis of articles published between 2000 (01/01/2000) to 2023 (04/16/2023) on chlorides in the oil industry. The analysis identified the contributions of researchers from various countries, institutions and future trends.

2.1 DATABASE

Web of Science (WOS) was chosen to conduct the research because it is considered a comprehensive database and ideal for bibliometric analysis. The following terms were used in the search queries for data collection: “Petroleum” OR “Crude oil”, “Chloride” OR “Chlorine, “Measurements” OR “Determination”. The period chosen for analysis was from 01/01/2000 to 04/16/2023. All data were collected on April 16, 2023 to avoid changes in the number of publications and citations. The “Topic” form of advanced search in WOS was used (Search the title, abstract, the author's keywords and Keyword Plus). As this article seeks to examine the current status and trends in research, only articles from peer-reviewed research journals were used for the analysis.

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2.2 Data performance analysis

In total, 100,574 publications met the selection criteria. These documents were categorized into four main types: articles (82,626, 82.1%), conference articles (13,778; 13.7%), reviews (3699; 3.7%) and others (502; 0.5%). In this study, only "article" type was considered, as article citation data was a more reliable reflection of search bias. A refined search using the keywords "Chloride" OR "Chlorine" and "Measurements" OR "Determination" resulted in 1362 records (articles, conference and review articles) and, restricting to articles only, 222 records. From the group of 222 articles, an extended search was performed in WOS, resulting in 3687 records. The WOS extended search includes the articles and the different types of citation of this article (article, review, conferences and others). From this group, only articles were selected, resulting in 3117 records without self-citations (H-index 38). The database with the group of 222 and 3117 articles were exported in "plain text" format, which included "full record and cited references" information for later interpretation and visualization using bibliometric analysis software.

2.3 Software selection

For this bibliographical analysis, the VOSviewer application (VOSviewer version 1.6.19) and Microsoft Excel software Microsoft Office 365) were chosen. The VOSviewer bibliometric application was chosen because it is free and available on the internet (https://www.vosviewer.com/) and is widely used. This app was developed by Leiden University to assess the current landscape and research hot spots in a field of science. This app allows visual analysis of published literature by country, research institution and keyword (Van Eck & Waltman, 2010). the software VOSviewer has advantages such as displaying co-occurrence clustering and ease of use (Biresselioglu et al., 2020). VOSviewer builds maps based on a co-occurrence matrix. The construction of a map is a process that consists of three steps: (i) a similarity matrix is calculated based on the co-occurrence matrix; (ii) a map is built by applying the VOS mapping technique to the similarity matrix; (iii) the map is translated, rotated and reflected (Van Eck & Waltman, 2010). When creating the bibliometric map, the frequency of keywords was defined and less relevant keywords were excluded. The software VOSviewer uses terminology to present the descriptive analysis of the data. In this software , the word "item" defines the objects of interest (publications, researchers or terms); grouping is a set of items included in a map *;* occurrence corresponds to the number of times it appears in the search; link is a relationship or connection between two items that corresponds to the calculated nodes which, in turn, indicates the degree of correlation; link strength represents a positive numerical value of the strength of a link, and the greater this value, the greater the strength represented by the item. The thickness of the line connecting two items (link) represents the intensity of cooperation (Van Eck & Waltman, 2010).

Data exported from WOS were handled by Microsoft Excel and VOSviewer. The number of publications (by year, country, institution and journal) and the annual variation trend of publications (by year and main countries), as well as highly cited literature, were analyzed in

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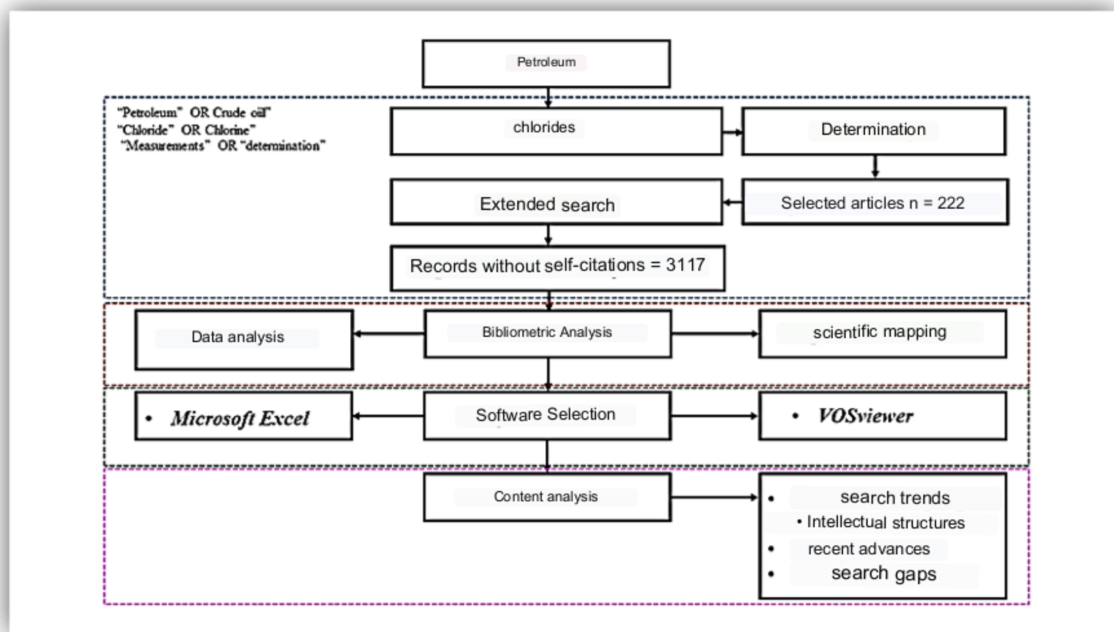
Microsoft Excel. The analysis of co-authorship and co-occurrence relationships was implemented by VOSviewer.

2.4 Data analysis strategy

The strategy used for the bibliometric analysis of this study was divided into three stages. In the first stage, a search was performed on the Web of Science Database with previously established keywords. The data obtained were archived for statistical treatment. In the second stage, data mapping was carried out to eliminate duplicity, standardize spellings, among others. Next, the data were processed using Excel and VOSviewer software. In the last step, the results were analyzed to identify trends, intellectual structures, recent advances and possible research gaps. The strategy flowchart is described in Figure 1.

Figure 1. Analysis flowchart used in this study.



Source: Authors (2023)

3 RESULTS AND DISCUSSION

3.1 Evolution of the number of publications

The first records in the scientific literature on techniques for determining chlorides in petroleum and their fractions were found in the period from 1957 to 1959. In 1957, Granatelli G. proposed the methodology using combustion and determination by potentiometry (Granatelli, 1957), and YAO and Porsche (1959) adapted the X-Ray Fluorescence technique for the determination of chlorides and sulfur in petroleum fractions (Yao & Porsche, 1959).

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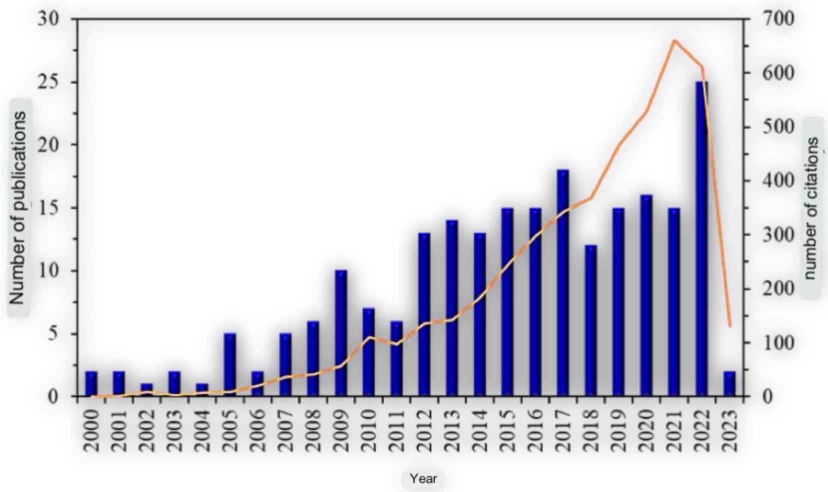
Considering the importance of chloride determination in the petroleum industry, a bibliometric analysis of publications and citations over the last 23 years was performed to identify relevant perspectives and research topics in the area. Initially, an analysis was performed only on the group of 222 articles that met the established criteria. From 2000 to 2023, it was possible to observe a 92% increase in the number of publications and citations on the determination of chlorides in oil (Figure 2). From 2012 to 2018, 100 articles were published with an average of approximately 245 citations. However, from 2019 to 2021, there was stability in the number of publications (average of 15 articles), which may be related to the effects of the pandemic caused by the SARS-CoV-2 virus, which impacted research activities in laboratories. In 2022, a peak of publications was recorded with 25 articles, indicating that the topic of chloride determination still deserves attention from scientific research.

Figure 2. Annual numbers of publications and citations related to the determination of chlorides in petroleum in the Web of Science database during the period 2000 to 2023



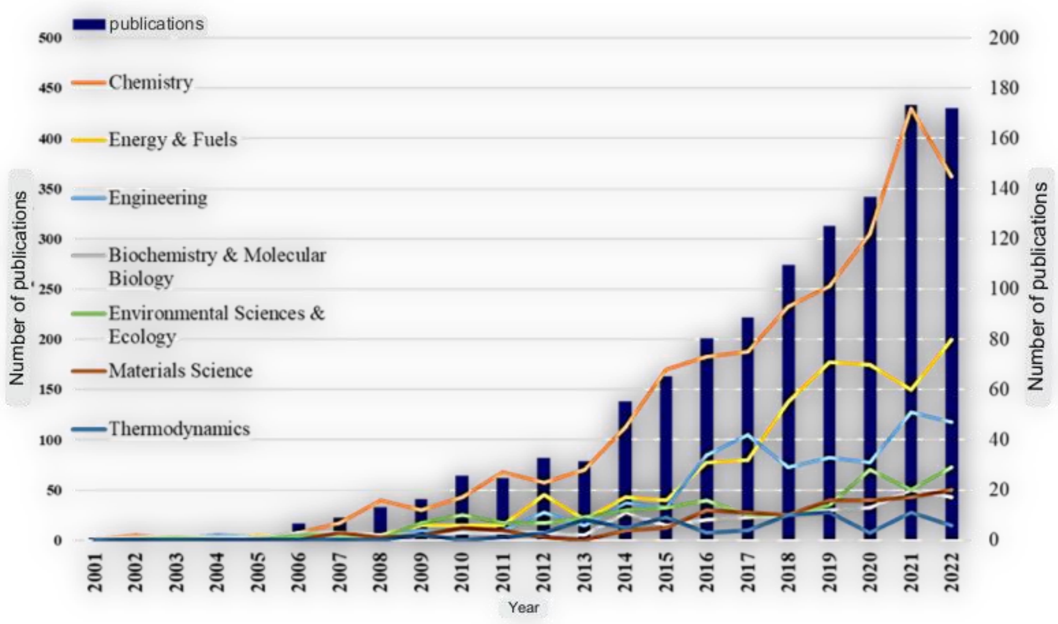
Source: Authors (2023)

In 23 years of publications in this field, the WOS extended search resulted in a total of 3687 records (articles, reviews, conferences and others). From this group, only article records were selected, resulting in 3117 records. As can be seen in Figure 2, there was an increase in citations over the period, indicating the importance of the topic.

The 222 selected articles and the 3117 records from the extended search were grouped to perform a more comprehensive analysis of the data. Duplicates and articles with incomplete information were excluded. Considering that the data for the year 2023 are still incomplete, they were not considered. The resulting database (3158 records) of this treatment was used for the next analyses.

WOS classifies publications in different areas of knowledge such as chemistry, engineering, thermodynamics, among others. To evaluate the distribution of journals by area, an investigation was carried out using the selected database (3158 records). In this group of publications, according to *WOS categories*, the most representative areas were: "*Chemistry*", "*Energy & Fuels*", "*Engineering*", "*Environmental Sciences & Ecology*", "*Biochemistry & Molecular Biology*", "*Material Science*". , "*Thermodynamics*", "*Science & Technology – Other Topics*", "*Polymer Science*" and "*Geochemistry & Geophysics*" (Figure 3). The "*Chemistry"* area leads the number of publications followed by "*Energy & Fuels*" and "Engineering", with a total of 1063, 512 and 339 records, respectively. The areas of "Environmental Sciences & Ecology" and "Biochemistry & Molecular Biology" occupy the fourth and fifth place with 210 and 138 records, respectively, showing an increase in environmental concerns. The areas of "Material Science" (133 records), "Thermodynamics" (78 records), "Science & Technology – Other Topics" (77 records), "Polymer Science" (57 records) suggest the importance of the theme for the development of new technologies. Finally, the area of "Geochemistry & Geophysics" (49 citations) can indicate efforts to develop technologies for unconventional oil and gas resources.

Figure 3. Evolution of the annual number of publications and relationship with the most representative research areas related to the determination of chlorides in petroleum, obtained from the *Web of Science* database during the period from 2000 to 2022.



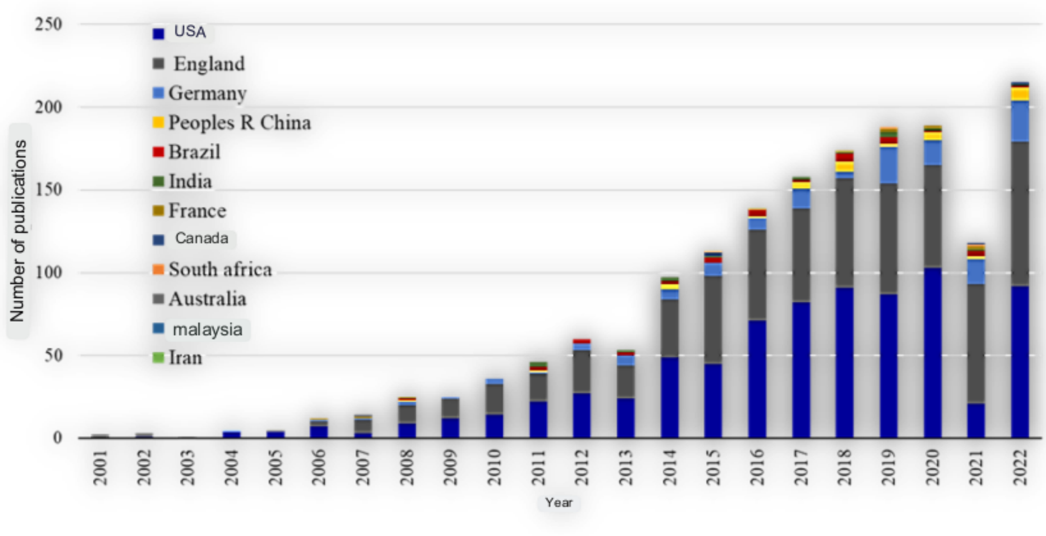
Source: Authors (2023)

3.2 INTERNATIONAL PRODUCTION AND COLLABORATIONS

Country production was broken down annually for the period 2000 to 2020 (Figure 4). The countries with the highest records were: "*USA*" (798), "*England*" (705), "*Germany*" (137), "*People R China*" (35), "*Brazil*" (32), "*India*" (16), "*France*" (11), "*Canada*" (3) and "*South Africa*" (3). In the period from 2000 to 2010, England and the United States were the countries that led the production, with 59 and 54 records, respectively, and the others had incipient production. From 2010 onwards, production increased until 2020, when in 2021 there was a 38% drop. In 2022, publication records returned to the 2019 rates, with an increase of 20%. In these results, the negative impact of the pandemic on scientific production in the area was evident.

In the studied period, Brazil starts the contribution with 01 record in 2008 and, the highest number in 2018 with 05 publications. In the intervals of 2007-2010, 2011-2014, 2015-2018, 2019-2022, the country produced 1, 9, 13 and 9 publications, respectively. These results can be attributed to the implementation of the legal framework for innovation (Federal Innovation Law No. 10,973/04) and the Royalties Law (Law No. 12,858 of 2013), which allocated a portion of oil and gas exploration to education areas Natural. Due to these laws, in 2002, the company Petrobras SA made investments in the research infrastructure of Brazilian universities. These investments resulted in a rapid growth of scientific and technological infrastructure and modernization of institutions (Bueno et al., 2017) . The investments resulted in favorable conditions for the development of national innovation systems with the objective of valuing internal resources and competing internationally. However, from 2017 onwards, the company began changing its business strategy and disinvesting in research and development programs and partnerships with universities (Schutte, 2021) . This new scenario may explain the decline in the production of articles in the period 2018-2022.

Figure 4. Evolution of the annual number of publications of the 10 countries with the greatest relevance related to the determination of chlorides in petroleum, in the *Web of Science* database during the period from 2000 to 2022.



Source: Authors (2023)

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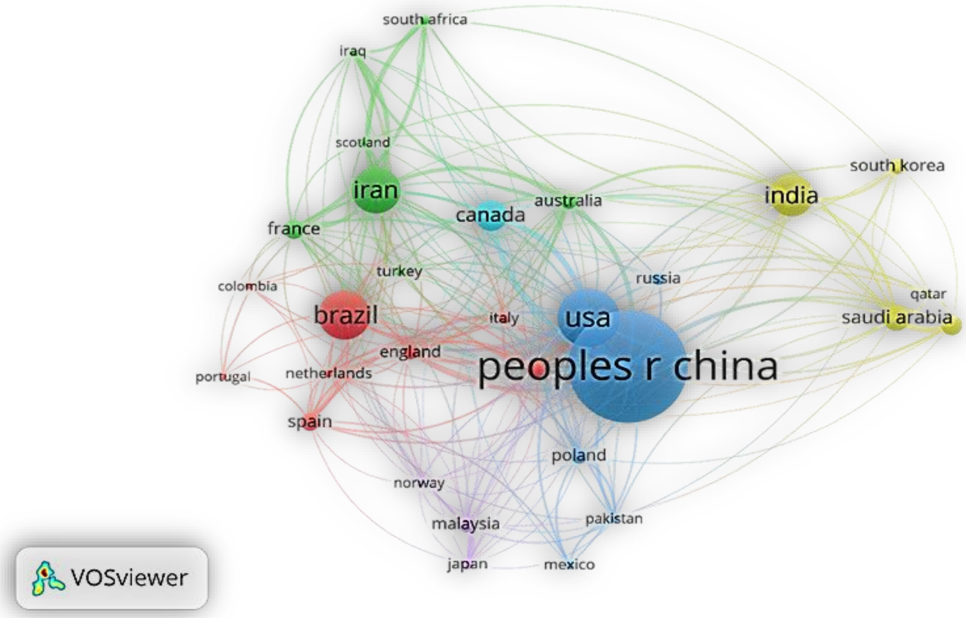
Research collaboration among leading countries on the topic of chlorides in petroleum was evaluated. The evaluation of international collaboration was carried out through bibliometric analysis applied to co-authorship and the number of publications limited to the established parameters. In this study, the 30 most productive countries were chosen (Figure 5). The size of the circles represents the frequency of occurrence in each country, and the curved lines show the *link strength* between the partnerships. The countries with the highest *link strength indexes* were: "*People R China*" (191), "*USA*" (187), "*Iran*" (144), "*Canada*" (113), "*Saudi Arabia*" (83), "*Australia*" (81), "*England*" (69), "*France*" (69), "*India*" (59) and "*South Africa*" (57).

Figure 5. Network visualization map of the research collaboration among the top 30 countries in the number of records related to the determination of chlorides in petroleum, in the *Web of Science* database during the period 2000 to 2022. The lines show research collaboration between connected countries. Node size is indicative of international research collaboration for that country. Similar color indicates close search interest.



Source: Authors (2023)

3.3 Distribution of publications in journals

The selected dataset of 3158 articles was used to analyze the panorama of publications in journals. The result showed that the articles were published in 128 journals indexed in WOS. Table 1 lists the 10 journals with the highest number of publications. In this selected group, only 02 journals are open access. The *H-Index* and Impact Index (IF) range from 111-237 and 4.0-10.7, respectively, indicating that they are relevant journals in academia. The journals *Energy & Fuels* and *Journal of Molecular Liquids* had the highest number of publications with 173 and 155, respectively. In addition, the journals are from different areas such as chemistry, engineering, environmental and thermodynamics, corroborating the results of categories in the area.

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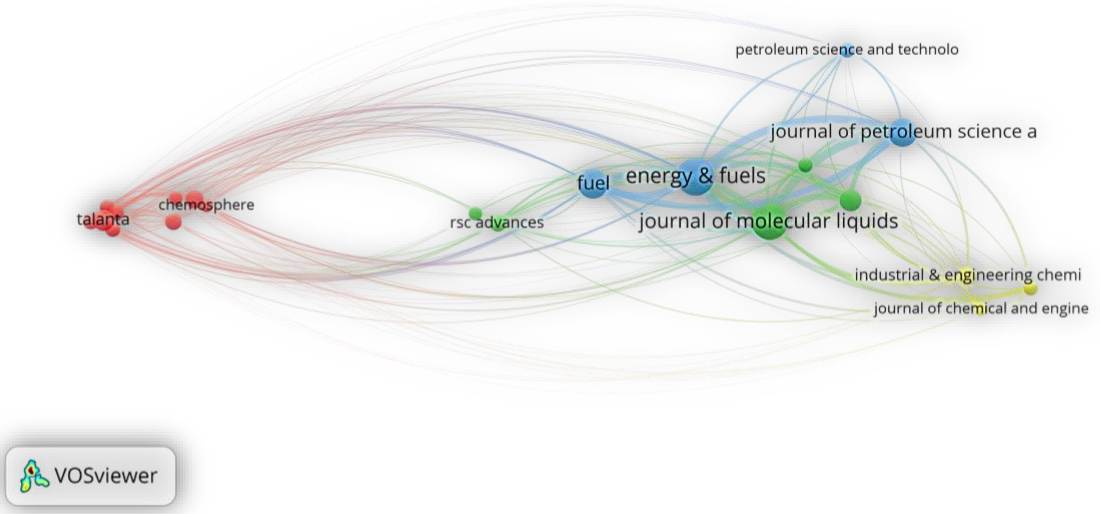
Table 1. Group of 10 journals indexed in *Web of Science* with the highest number of publications described in the selected database, in the period 2000-2022.

Rank	Journal	Total Publications	Country	IF*	*H-Index*	Open Access
1	*Energy & Fuels*	173	USA	4,654	186	No
2	*Journal of Molecular Liquids*	155	Netherlands	6,633	111	Yes
3	*Fuel*	104	Netherlands	8,035	213	No
4	*Journal of Petroleum Science and Engineering*	101	Netherlands	4,97	122	No
5	*Colloids and Surfaces a-Physicochemical and Engineering Aspects*	60	Netherlands	5,518	170	No
6	*Talanta*	54	Netherlands	6,556	161	No
7	*Science of The Total Environment*	40	UK	10,75	244	No
8	*Industrial & Engineering Chemistry research*	36	USA	4,326	221	No
9	*Journal of Chromatography A*	34	Netherlands	4,601	237	No
10	*RSC advances*	33	UK	4,036	148	Yes

IF: Impact Factor

Of the 128 journals found in the data group, the 20 with the highest number of publications were selected to assess correlations (Figure 6). As can be seen, 04 groups are formed, with emphasis on 03 journals with scope in petroleum, and 01 journal with scope in analytical chemistry. The journals *Journal of Molecular Liquids*, *Energy & Fuels*, *Journal of Petroleum Science and Engineering*, showed the highest *link strengths*, 27117, 24543 and 22122, respectively. It is noteworthy that the journal *Journal of Molecular Liquids* is open access and may have contributed to the strength of the *link strength*.

Figure 6. Visualization of the co-citation network of the most prominent journals related to the determination of chlorides in petroleum, in the *Web of Science* database during the period from 2000 to 2022. Circles with similar colors indicate a set of related journals. The highlight of the circles and texts in each grouping represents the strength of their co-occurrence, while the distance of the elements and lines show the relationship and connection between the different journals, respectively.



Source: Authors (2023)

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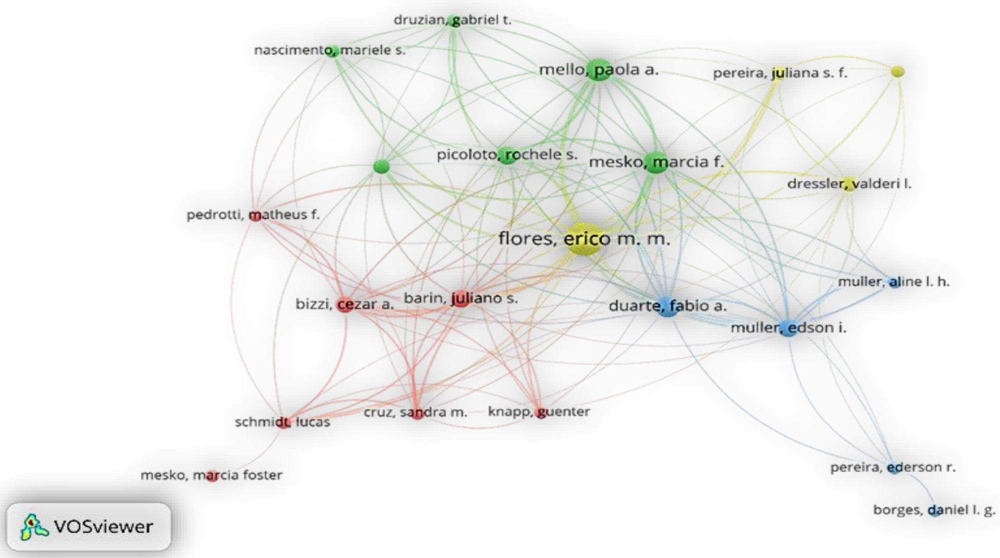
3.4 Analysis of citation and authorship in the determination of chlorides in petroleum

The citation search identified 11634 authors and 10% of this group of authors were selected. 04 groups with 22 items were formed (Figure 7). The authors with the highest *link strength* for citation were: Flores, Erico MM (217), Mello, Paola A. (97), Mesko, Marcia F. (92), Duarte, Fabio A. (74), Picoloto, Rochele S. (63), Barin, Juliano S. (62), Bizzi, Cezar A. (58), Muller, Edson I. (54), Manshad, Abbbas khaksar (52) and Goto, Masahiro (51). The author Flores, Erico MM, had the highest number of citations (1524) and documents (72) and 49.3% more citations than the second highest ranked author. The first eight authors are Brazilian and from the Federal University of Santa Maria (UFSM). This group pioneered the determination of chlorides using microwave extraction and inductively coupled plasma mass spectrometry (*Inductively coupled plasma mass spectrometry* - ICP-MS). The authors Nascimento, Mariele S., Druzian, Gabriel T. and Pedrotti, Matheus F., also from the UFSM group, are grouped in the period 2016-2018, indicating that *link strength* may increase.

Figure 7. Visualization of the co-citation map of the most prominent authors in the number of records related to the determination of chlorides in oil, in the *Web of Science* database during the period from 2000 to 2022. The thickness of the lines connecting two authors indicates the accumulation of co-authorship (thicker lines mean more published articles), and the color groupings illustrate groups of authors with a high level of collaboration.



Source: Authors (2023)

The analysis results showed that China led the global production and collaboration while Brazil led the *ranking* of researchers with the highest number of citations. These results can be explained by the database construction criteria. Once the articles that met the keyword criteria (222) were selected, an extended search was carried out in WOS (3117) and the citations of the respective articles were included in the database. The database selected for the analyzes is the result of this set of records. This strategy was adopted to show which researchers lead the *ranking* and the origin of the productions that cite the author. Therefore, the innovation and relevance of Brazilian scientific works is evidenced by the high number of citations by researchers from other countries.

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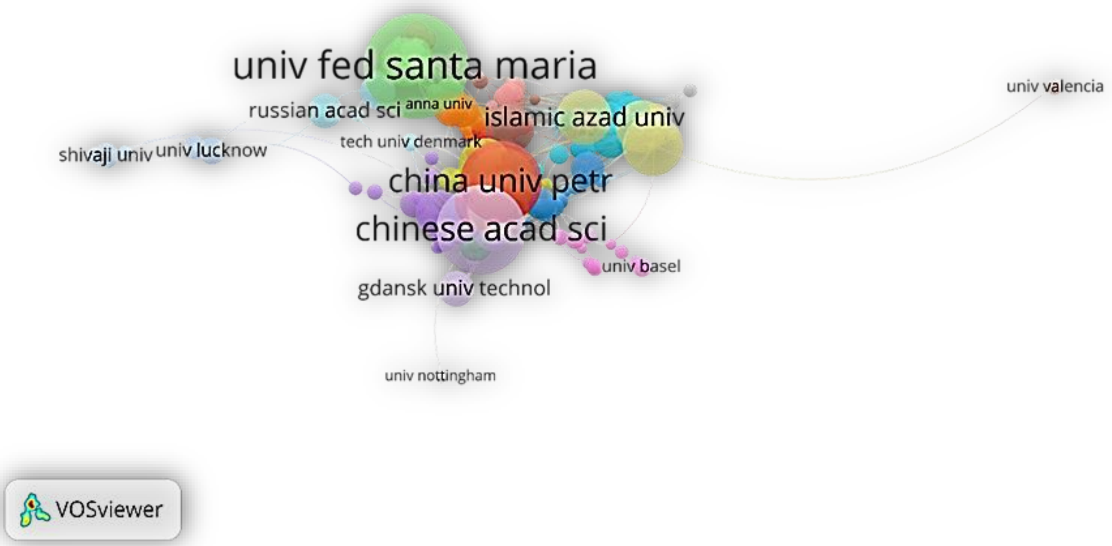
An analysis of the institutions with the greatest impact on research on the determination of chlorides in petroleum was carried out. The database had a total of 2782 institutions and only 227 institutions were selected. The institutions with the highest *link strength* were: Federal University of Santa Maria (Brazil) (88), *Chinese Academy Sciences* (China) (86), *Islamic Azad University* (Iran) (59), *University of chinese Academy of Sciences* (China) (59), *Shiraz University* (Iran) (57), *Sharif University of Technology* (Iran) (55), *University Kwazulu-Natal* (South Africa) (54), *China University of Petroleum* (China) (52), Federal University of Pelotas (Brazil) (45) and *Universiti Teknologi Petronas* (Malaysia) (39) (Figure 8). Corroborating the results of higher citations, Brazil contributed with 02 institutions, showing the relevance of this research developed in the country. China and Iran contributed with 03 institutions, respectively. Considering that China and Iran are listed among the largest oil producers in the world, 6th and 8th respectively, it may be strategic for these countries to develop technologies in the oil sector.

Figure 8. Visualization of the network of occurrences of the most prominent institutions in the number of records related to the determination of chlorides in oil, in the *Web of Science* database during the period 2000-2022. The thickness of the lines that connect the organizations indicates the accumulation of co-authorships (thicker lines mean more articles published together), and the color groupings highlight the groups of institutions with a high level of collaboration.



Source: Authors (2023)

3.5 Description of the most cited articles

The 10 most relevant publications using the scope and link strength values of this bibliometric analysis as the main parameter are shown in Table 2. Brazil is the only country that contributed to this group of articles. The publications were registered in the period from 2008 to 2015; but, due to the innovative nature of the research, they are references that guided the determination of chlorides in different types of samples in recent years. Link strength values are in the range of 24 to 141. The sample preparation methodologies used in these papers are microwave induced combustion (MIC), pyrolysis, liquid-liquid extraction, microwave and pyrohydrolysis. Chloride determination was performed by ion chromatography, inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass

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spectrometry with dynamic reaction cell (DRCICP-MS), inductively coupled plasma mass spectrometry (ICP-MS) and energy dispersive X-ray fluorescence (EDXRF).

Table 2. List of the 10 most cited articles in the Web of Science, described in the selected database on chloride determination in the period 2000-2022.

Rank	Title	Methodology	Publication Year	Journal	LST*	NC**
1	*Chloride determination by ion chromatography in petroleum coke after digestion by microwave-induced combustion*	Cromatografia de íons	2008	*Journal of Chromatography A*	141	62
2	*Chlorine and sulfur determination in extra-heavy crude oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion*	ICP-OES	2009	*Spectrochimica Acta Part B*	125	86
3	*Chlorine Determination in Petroleum Coke Using Pyrohydrolysis and DRC-ICP-MS*	DRCICP-MS	2008	*Atomic Spectroscopy*	88	26
4	*Feasibility of Microwave-Induced Combustion for Digestion of Crude Oil Vacuum Distillation Residue for Chlorine Determination*	ICP-OES e cromatografia de íons	2009	*Energy& Fuels*	86	48
5	*Heavy crude oil sample preparation by pyrohydrolysis for further chlorine determination*	ICP-OES e cromatografia de íons	2011	*Analytical Methods*	57	32
6	*Microwave-Assisted Procedure for Salinity Evaluation of Heavy Crude Oil Emulsions*	Cromatografia de íons	2010	*Energy& Fuels*	36	19
7	*Evaluation and determination of chloride in crude oil based on the counterions Na, Ca, Mg, Sr and Fe, quantified via ICP-OES in the crude oil aqueous extract*	ICP-OES	2015	*Fuel*	36	32
8	*Determination of chloride in brazilian crude oils by ion chromatography after extraction induced by emulsion breaking*	Cromatografia de íons	2016	*Journal of Chromatography A*	28	37
9	*Direct chlorine determination in crude oils by energy dispersive X-ray fluorescence spectrometry: An improved method based on a proper strategy for sample homogenization and calibration with inorganic standards*	Fluorescência de raios X por energia dispersiva	2011	*Spectrochimica Acta Part B*	24	21
10	*Measuring Salinity in crude oils: Evaluation of methods and an improved procedure*	Método de Mohr	2008	*Fuel*	24	27

LST*: *link strength* total
NC**: number of citations

The biggest article-link strength was “Chloride determination by ion chromatography in petroleum coke after digestion by microwave-induced combustion”, published in Journal of Chromatography A in 2008 (Pereira, et al., 2008). This article has a link strength value of 118. In this article, the authors used microwave-induced combustion to digest petroleum coke in closed vessels for subsequent determination of chloride by ion chromatography. Accuracy was

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evaluated using certified reference materials with 98% agreement, using water as the absorbent solution in the reflux step. The limit of quantification of the method was 3.8 µg g $^{-1}$ for chloride. The second major article -link strength (125) was "Chlorine and sulfur determination in extra-heavy crude oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion", published in the journal Spectrochimica Acta Part B (Pereira et al., 2009). This article also used the microwave-induced combustion methodology. The sample used for this investigation was extra heavy oil and the determination of chlorides by ICP-OES. The limits of detection by ICP OES was 12 µg g $^{-1}$ for chloride.

Chloride analysis in petroleum coke samples is strategic. Coke is a product of the petroleum refining process and the amount of chlorides in the sample depends on the origin of the petroleum. Many of the problems of corrosion and incrustation formation in the various refinery equipment are due to the presence of chloride salts and sediments in oil and its derivatives. Thermal decomposition of chloride salts deposited in refinery pipes, leading to the formation of hydrochloric acid, can cause corrosion in distillation equipment (Mitra et al., 2022; Speight, 2014). Coke is a product widely used as fuel, electrode manufacturing and other products. Contributing with a methodology for the determination of chlorides in this type of sample, the article "Chlorine Determination in Petroleum Coke Using Pyrohydrolysis and DRC-ICP-MS" is the third article with the highest link strength (88) (Antes et al., 2008). Published in the journal Atomic Spectroscopy in 2008, the authors propose a methodology using pyrohydrolysis for the decomposition of petroleum coke (with low chlorine concentration) and chlorine determination by inductively coupled plasma mass spectrometry with dynamic reaction cell (DRCICP-MS). The quantification limit for chlorine in petroleum coke was 3.9 µg g $^{-1}$.

Petroleum Vacuum Distillation Residue (RDV) are samples related to the bottom products of the distillation process. The determination of chlorides in RDV is of great concern for process control in oil refineries. The Feasibility article of Microwave-Induced Combustion for Digestion of Crude Oil Vacuum Distillation Residue for Chlorine Determination proposed a method to determine chlorine for RDV (Pereira et al., 2009). This was published in the journal Energy & Fuels and has a link strength value of 86. The authors used the microwave induced combustion (MIC) method for the digestion of RDV and subsequently determined chlorine by ICP-OES and ion chromatography. According to the authors, the samples used in the investigation were enriched with certified reference material (BCR 181 and NIST 1634c) and chlorine recovery was observed in the range of 98.4 to 100.2%.

Considering the complexity of heavy oil samples, another methodology was proposed for chloride determination. the article "Heavy crude oil sample preparation by pyrohydrolysis for further chlorine determination" (Antes et al., 2011) developed a method for determining chlorine in heavy oil using pyrohydrolysis for sample decomposition. Chlorine was determined using ion chromatography and ICP-OES. According to the authors, the precision was evaluated by analysis of certified reference material (NIST 1634c) and the results obtained were consistent with the ASTM D6470 method. Considering the importance of heavy oil, another methodology for determining chlorides in this type of sample was described in the article "Microwave-Assisted Procedure for Salinity Evaluation of Heavy Crude Oil emulsions" (Moraes et al., 2010). In this article the authors used a procedure for extracting salts from emulsions produced by heavy oil and applied microwave radiation. Chloride determination was performed by ion chromatography and the described extraction efficiency was greater than 95%.

The article "Evaluation and determination of chloride in crude oil based on the counterions Na, Ca, Mg, Sr and Fe, quantified via ICP-OES in the crude oil aqueous extract" presented another strategy for chloride determination (Souza et al., 2015). The authors quantified the major chloride counterions (Na, Ca, Mg, Sr, and Fe) using ICP-OES after hot solvent extraction using the modified ASTM D6470 method. The authors observed a concordance of results between the potentiometric titration and ICP-OES methods.

The "Determination article of chloride in Brazilian crude oils by ion chromatography after extraction induced by emulsion breaking" (Robaina et al., 2016) presented another approach for the determination of chlorides. The authors developed an extraction method induced by breaking an oil/water emulsion for the determination of chlorides in petroleum. The determination of chlorides was performed by ion chromatography. According to the authors, the limit of detection and quantification was 0.5 µg g^{-1} NaCl and 1.6 µg g^{-1} NaCl, respectively.

Considering the simplification of the analytical process, the article "Direct chlorine determination in crude oils by energy dispersive X- ray fluorescence spectrometry: an improved method based on a proper strategy for sample homogenization and calibration with inorganic standards" was described by Brazilian authors (Doyle et al., 2011). In this paper, a methodology was proposed to quantify low concentrations of chlorine in petroleum using energy dispersive X-ray fluorescence (EDXRF). According to the authors, the method presented a linear response that covered the range of 8 to 100 µg g^{-1} of chlorine.

The microwave technique is also used in the "Measuring article Salinity in crude oils: evaluation of methods and an improved procedure" (Fortuny et al., 2008) . The authors used the strategy of forming a water/oil emulsion and then breaking it by microwave irradiation to measure the salinity of the wash water. The salt was characterized by Mohr 's method.

The selection of the group of articles corroborates the results of the most cited authors and institutions, considering that six articles are co-authored by researcher FLORES and originate from UFSM. This group of ten articles with the highest link strength values illustrates the challenge of determining chlorides in complex samples such as oil. With regard to instrumentation for the determination of chlorides, the complexity of the oil matrix presents considerable limitations for the application of current analytical technology (Gajdosechova et al., 2021; Flores et al., 2020). The emergence of new types of oil and technical limitations of the equipment, despite the proposed methodologies, indicate that the determination of chlorides in this matrix is still a subject for development and innovation.

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3.6 EMERGING AND MORE CO-OCCURRING KEYWORDS

Keywords are highly concise terms that are related to the content of a research or article. The statistical evaluation of keywords is an important tool for identifying relevant research topics and perspectives for a research field, in addition to being essential for monitoring the development of science (Li et al., 2018). In the database, 7137 keywords of authors were found and, from this set, the 10 keywords with the highest co-occurrence were selected (Table 3). The keywords "interfacial- tension", "enhanced oil-recovery", "ionic liquids", "adsorption", "surfactant" and "crude oil" showed the highest co-occurrences and link strength. The keywords with the highest co-occurrence are present in articles in the field of oil recovery.

World oil production currently comes largely from mature and declining fields. To meet demand, producers can increase production in oil fields or develop new reservoirs. Typically, primary and secondary oil recovery exploits less than half of the site's original oil. Due to rock wettability, heterogeneity and well patterns, residual oil still exists and advanced oil recovery techniques are developed for this purpose. Various chemicals such as polymers, surfactants, salts and alkalis, ionic liquids are applied in oilfields for oil recovery (Jafarbeigi et al., 2023). New materials such as nanoparticles and nanocomposites have also shown potential (Liu et al., 2021). Most of these materials alter the oil-water interfacial tension or the wettability of the rock or both (Al-Azani et al., 2022). Therefore, there are still many challenges that need to be overcome in the area of advanced oil recovery and the selection of keywords corroborate this research trend by researchers.

Table 3. Author keyword group with highest co-occurrence and link strength in Web of Science, described in the selected database on chloride determination in the period 2000-2022

Rank	Keyword	Co-occurrences	*Link Strenght*
1	*Interfacial-tension*	149	371
2	*Enhanced oil-recovery*	127	305
3	*Ionic liquids*	116	195
4	*Adsorption*	80	158
5	*Surfactant*	74	164
6	*Crude-oil*	64	111
7	*Asphaltene*	59	116
8	*Wettability alteration*	59	144
9	*Acrylamide*	58	48
10	*Heavy crude-oil*	53	100

The network analysis of the keywords presented 8 groupings and distributing them in connections and period 2014-2020 (Figure 9). A complex and close relationship was formed between the keywords. Each circle represents a keyword, and the size of the circle reflects the number of co-occurrences of a keyword. The connection means a co-occurring relationship between two keywords, and the color represents the keyword grouping (search topic). The largest cluster contains 24 items and contains keywords such as "*acrylamide*", "demulsification", "heavy crude-oil" and "emulsions". The second largest cluster (19 items) contains keywords such as "corrosion", "corrosion inhibition" and "adsorption". The third largest cluster (14 items) contains keywords such as "cellulose", "gas-hydrate", "ilica" and

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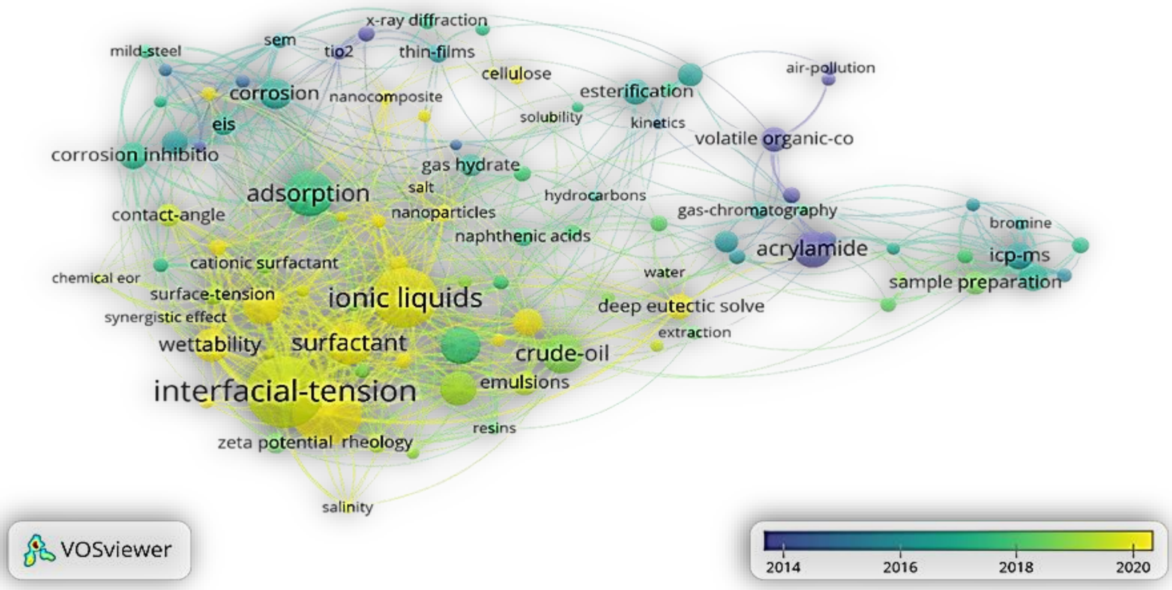
"electrolytes". The grouping that contains the highlighted items in the period of 2019 and 2020 includes the keywords "chemical enhance oil recovery", "contact-angle", "enhanced oil-recovery", "interfacial- tension", "salinity", "mart water", "surfactant flooding", "wettability" and "wettability alteration" (Figure 9). This set of keywords are related to advanced oil recovery processes Jafarbeigi et al., 2023). This result suggests that these keywords will possibly be the research topics for technological and sustainable advances in the oil recovery process (Mariyate et al., 2023).

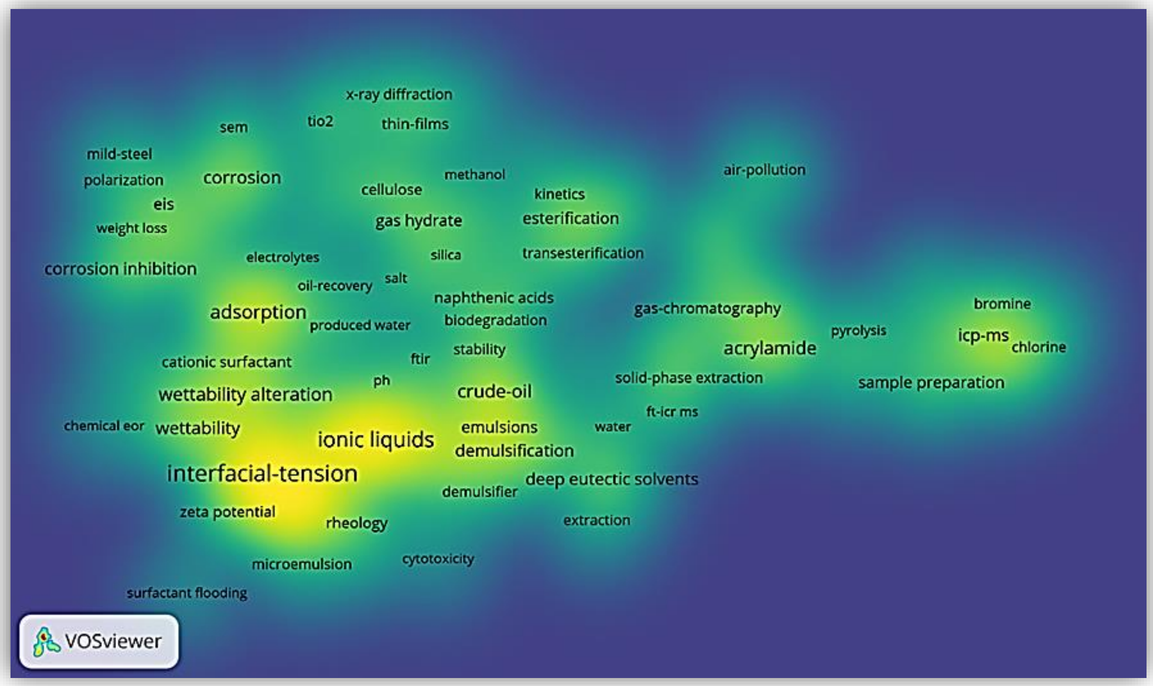
Figure 9. Network of occurrences of author keywords with greater prominence in the number of records related to the determination of chlorides in oil, in the *Web of Science* database during the period 2000-2022. Circles with similar colors indicate a set of related keywords. The highlight of the circles and texts in each cluster represents the strength of their co-occurrence, while the distance of the elements and lines show the relationship and connection between the different keywords, respectively.



Source: Authors (2023)

The analysis of the keywords suggests that the focus of the research is on topics related to oil recovery and its challenges. The identification of emerging and more frequent terms and topics is the key to understanding the development of a field of research. As the research area develops, researchers carry out intense work to generate and accumulate knowledge. Consequently, this strategy results in the maturation and growth of a certain area. Identifying the hot spots of a search domain helps you track trends and better understand the field. Figure 10 presents the hottest terms, which are general terms like surface tension, ionic liquids, emulsion, demulsification, adsorption, zeta potential, and wettability. It is observed that other words are less used, indicating a decrease in priority in the investigation of these research topics. The font size of terms represents the relative advance and meaning of a term.

Figure 10. Density visualization for keywords identified in publications in the *Web of Science database* in the period 2000-2022, related to the determination of chlorides in petroleum. Progressive increase in density is indicated by a deeper yellow color. More intensely colored dots indicate a higher number of keyword occurrences.



Source: Authors (2023)

4 FINAL CONSIDERATIONS

In this study, bibliometric analysis was performed on a total of 3339 articles related to the determination of chlorides in petroleum in the period from 2000 to 2023. A constant increase was observed in the production of publications, with extensive international collaboration in the last 23 years. The growth rate of the number of articles published from 2000 to 2019 was 92.0%. In 2021, there was a decrease of approximately 37.0% in the production of articles, which can be attributed to the effects of the pandemic.

The results of the bibliometric analysis indicated that research on the application of chloride determination is growing, with an annual increase in publications in the area. In addition, it identified that the theme is interdisciplinary, with publications in different areas of knowledge. China leads global production and collaboration. Brazil leads the ranking of researchers with the highest number of citations. Therefore, the innovation and relevance of Brazilian scientific works is evidenced by the high number of citations by researchers from other countries. The emerging keywords were: surface tension, ionic liquids, emulsion, demulsification, adsorption, zeta potential and wettability. This group of terms suggests that research efforts are focused on the advanced oil recovery area.

The use of only one database may be a limitation of this bibliometric study. Relevant publications that are not registered with the WOS may have been disregarded. In future research, it is suggested to expand the search using two or more databases. In addition, it is recommended to use text processing tools to objectively filter the information.

This bibliometric analysis can help researchers understand the current knowledge landscape in the field of petroleum chloride determination and guide future research agendas. The challenges for the analytical determination of inorganic chlorides can be an opportunity for the development of new technologies and research topics.

5 ACKNOWLEDGMENT

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