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# 18 Year analysis of RASFF notifications on Sudan dye adulterated cases in palm oil (2004 to 2022) and the principles of the technique for its detection

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Palm oil is one of the most widely consumed food products globally. Despite the restriction of Sudan dyes as a food colouring agent, these dyes still feature prominently in palm oil adulteration, which occurs in most developing countries. The current study aims to provide insight into the recent palm oil adulteration over 18 years and the methods for detecting this adulterant. By using the European Union's (EU) rapid alert system for food and feed (RASFF), data on palm oil adulterated with Sudan dye was extracted between the years 2004 to 2022 and analysed to determine their overall pattern. Adulteration of palm oil was categorised by the origin and concentration of various Sudan dyes. The results from RASFF could confirm a total of 204 cases of Sudan dye adulteration in palm oil. African countries recorded the highest number of alerts for exporting palm oil adulterated with Sudan dye to European countries. Additionally, 70 reported cases of palm oil adulteration were recorded in 2004 and this was a result of increased regular testing of Sudan dyes in foods within the EU community. Also, the concentration of Sudan IV dye was the highest in all the palm oil tested by the notifying countries, since it is highly soluble in crude palm oil compared to Sudan I, Sudan II and Sudan III. Finally, the results presented in this manuscript highlight the importance of the detection of Sudan dye adulteration in palm oil from 2004 to 2022 from the RASFF database. The techniques frequently used for analysing palm oil included gas chromatography mass spectrometry (GC-MS), gas-liquid chromatography (GLC), reversed-phase high-performance liquid chromatography (RP-HPLC), high performance liquid chromatography (HPLC), differential scanning calorimetry (DSC), NIR spectroscopy, MIR spectroscopy, FTIR spectroscopy, Raman spectroscopy, surface enhanced Raman spectroscopy (SERS), and electronic tongue. Among the methods reviewed, HPLC and GC-MS were frequently used; however, rapid non-destructive methods such as spectroscopic techniques for the onsite Sudan dye detection in palm oil would be very beneficial for many palm oil-producing countries in Africa.

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## Sustainability spotlight

An 18-year analysis of RASFF notifications of adulterated palm oil (2004 to 2022), combined with recent advances in detection methodologies, provides the necessary information to move towards novel sustainable detection techniques, other than the use of wet chemistry analytical methods. These well-known methods such as gas chromatography mass spectrometry (GC-MS), gas-liquid chromatography (GLC), reversed-phase high-performance liquid chromatography (RP-HPLC), and high-performance liquid chromatography (HPLC), and differential scanning calorimetry (DSC), are not sustainable, especially in developing countries where most of the palm oil is produced. Developing novel handheld techniques that do not involve chemicals or laboratory conditions such as NIR spectroscopy, Raman spectroscopy and SERS, offers a more sustainable approach to reducing the threat of food fraud in Africa. Palm oil is one of the most widely consumed food products in the world. Despite restrictions on the use of Sudan dyes as a food colouring, these dyes still play a major role in the adulteration of palm oil, which occurs in most developing countries. Portable analytical methods for Sudan dye adulteration could be the way forward for detecting palm oil adulteration onsite in developing countries in a more sustainable manner.

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## 1. Introduction

In recent years, the production and export of palm oil has increased more than other vegetable oils on the world market. As of February 2023, the scale of palm oil production was 77 million tonnes as compared to soybean oil, rapeseed oil and sunflower oil with 61 million metric tonnes, 32 million metric tonnes and 21 million metric tonnes, respectively. The



remaining vegetable oils make up less than 10 million metric tonnes, which indicates that palm oil is the leading vegetable oil, in terms of production.

Palm oil is one of the most widely used edible oils in West African countries and is also used globally as an ingredient in many food blends. Palm oil is known to have many nutritional and health benefits. It is used in some communities to treat conditions such as vitamin A deficiency due to its high carotenoid content.<sup>1</sup> Other uses include, manufacturing margarine, soap, detergents and in biofuel production. Palm oil is widely used in the food sector and is present in most ready-to-eat foods compared to other edible oils in Africa.<sup>2</sup>

Palm oil is obtained by extracting oil from the fleshy mesocarp of the palm fruit, which is known for its oil production. Depending on the structure of the fruit, palm fruit is divided into three varieties: *Pisifera*, which has a thin shell and rarely produces embryos; *dura* which has a thick shell and less mesocarp; and the commercially grown *tenara*, a D-P hybrid with a thin shell, more mesocarp and higher oil content.<sup>3</sup> Palm oil obtained from the palm fruit is in its crude form, and this is refined by physical methods such as degumming pre-treatment, bleaching, and the application of high temperatures and low pressures. This process helps to achieve purity characteristics such as acidity and the desired colour in edible oil.<sup>4</sup> Bleaching of crude oil produces a light-coloured oil of acceptable quality, as it removes the organic compounds that give the oil its undesirable colour.<sup>5</sup>

The orange-red colour of crude palm oil is due to the presence of carotenoids and other naturally occurring red pigments. However, during palm oil processing, the natural red colour of palm oil is reduced. To maintain the appearance, stability and sensory quality of palm oil, palm oil traders add food colouring to improve the colour, giving it a more reddish characteristic. Some of the food dyes used include Sudan dyes I-IV and azo dyes.<sup>1</sup> With the high global demand for palm oil, these dyes have increased and are used to adulterate lower quality palm oil. From the family of Sudan dyes, Sudan IV is most commonly used as a colouring agent to mask the paler colour of poor-quality palm oil and give it a more reddish appearance.

Sudan dyes (I-IV) are lipophilic azo dyes and are used as colouring agents in most industries to colour tiles, paints, waxes, and textiles and are also used to colour lipids.<sup>6,7</sup> Sudan

dyes are synthetic azo dyes that are banned for human consumption due to their carcinogenic and mutagenic effects, as classified by the International Agency for Research on Cancer (IARC).<sup>8</sup> However, some fraudulent traders may add them to palm oil to improve its colour and appearance. Sudan dyes are considered a serious threat to human health due to their carcinogenicity and are currently banned for use as food colourants.<sup>9-11</sup> Despite the ban on the use of azo dyes, including Sudan dyes, by the European Union (EU) and more restrictive laws in the United States of America (USA)<sup>12,13</sup> they are still being used by many countries to adulterate foods including palm oil. The widespread use of these dyes is to make the red colour of palm oil more apparent. Most people perceive a higher quality oil to be deeper red. Visual inspection of oil colour is a very important way to assess the oil quality in most developing countries. The Food and Drug Authority (FDA) in Ghana had alerted the general public to the adulteration of palm oil with Sudan IV dye when 98% of randomly sampled palm oils from 10 major markets in the Greater Accra Region, Ghana, tested positive for Sudan IV dye.<sup>14</sup>

Although there has been extensive research into the detection and authentication of palm oil, the detection of palm oil adulteration within the supply chain is challenging. To help monitor palm oil adulteration issues within the food supply chain, there are regulatory bodies that perform checks to predict and identify risks.<sup>15</sup> This study aims to provide an insight into the historical and recent notifications of palm oil adulteration over an eighteen year period (2004–2022) using the rapid alert system for food and feed (RASFF). The review will also discuss the methods used for analysing palm oil adulteration with Sudan dyes such as, the traditional wet chemistry methodologies and the emerging novel techniques.

## 2. Approach

### 2.1 RASFF data collection

Data was extracted from the RASFF online portal (European Commission, 2022) from July 2004 to December 2022. The RASFF database is updated daily and is stored on the Communication and Information Resource Centre Administrator (CIRCA) server at the Commission. The RASFF serves as an access database that provides information on specific

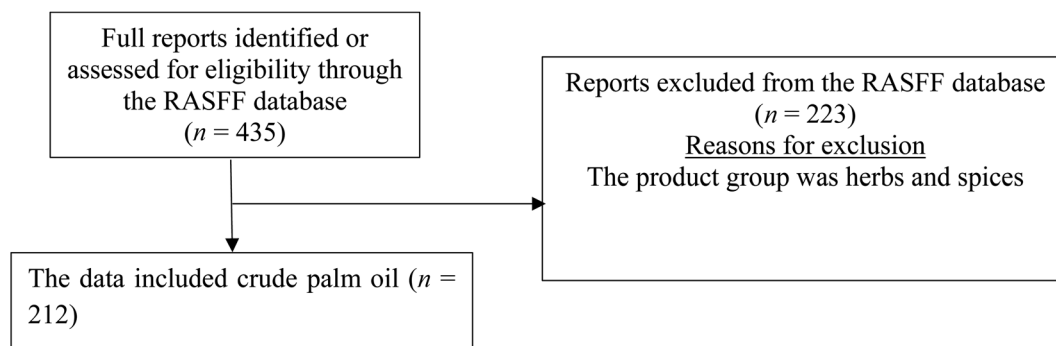


Fig. 1 PRISMA diagram of the study inclusion and exclusion process.



products, such as the date of notification, the country of notification and origin, the level of contaminants detected in the product and the hazard(s) identified.

The following criteria were used in the search of the RASFF online portal as shown in Fig. 1 using the PRISMA diagram:

1. Product group: fats and oils.
2. Keyword: Sudan dye.
3. Notification, type, risk decision and hazard: were left clear to include all notifications relating to the product categories.

## 2.2 Data analysis

The selected data relating to palm oil or palm crude oil were transferred to Microsoft Excel 2016 (Microsoft Corp., Redmond, USA) to generate descriptive statistics. The total number of notifications relating to palm oil adulterated with Sudan dye was determined. The reported Sudan dye concentrations in the palm oil samples were summarized and reported as  $\text{mg kg}^{-1}$  (ppm). An average value was calculated when more than one concentration was reported in a notification and the minimum and maximum concentration were given.

## 3. Results

### 3.1 Country of origin of palm oil adulteration

A total of 204 cases of palm oil adulteration with Sudan dyes from 2004 to 2022 were selected for analysis from the RASFF database. Among all the countries exporting palm oil to the EU, Africa recorded the highest number of cases of palm oil adulteration with Sudan dyes. For decades, Ghana has been known as the main African country for crude palm oil exports to the EU. In addition to Ghana, other West African countries such as Nigeria, Senegal, Guinea, Guinea-Bissau, Togo, Mali, Sierra Leone, Cote d'Ivoire and Gambia, were also found to be exporting adulterated palm oil.

Additionally, the results obtained indicated that some cases of palm oil adulteration with Sudan dyes originated from European countries such as the United Kingdom (UK), Netherlands, Belgium and France. However, these countries are not known to be palm oil producers, according to the FAO report on palm oil adulteration in 2022. The report also highlights that most cases of palm oil adulteration in France and Belgium were recorded during the early stages of testing between 2004 and 2005. The Netherlands is also known to have some of the largest ports in Europe. Therefore, many ships stop there to unload their cargo, which is then transported on to other parts of Europe. This may lead to higher notable incidences of food fraud in palm oil along the food supply chain since there are many more companies and people involved across borders, before the oil reaches the end consumer. The FAO's report on palm oil importers 2019 shows that Europe imports 11 million tonnes of palm oil, which is sourced from producing countries by major distributors based in Europe, where it is packaged and sold. There is currently no evidence of palm oil production in the UK, the Netherlands, Belgium and/or France. However, companies from these countries may be associated to palm fruit producing countries and therefore may still be involved in the palm oil production process.

### 3.2 Palm oil adulteration by continent of origin in the world

Of the 212 reports identified in the palm oil supply chain as being adulterated with various levels of Sudan dye, 171 were found to originate from Africa, as illustrated in Fig. 2 in percentage. The number of reported cases originating from Europe was 30, and 11 of the total number of cases had no reported country of origin (unknown origin).

### 3.3 Number of notification reports per year

Adulteration of palm oil for economic gain is believed to be common practice, as consumers are known to prefer palm oil with a redder colour. Fig. 3 shows the total number of reported cases of

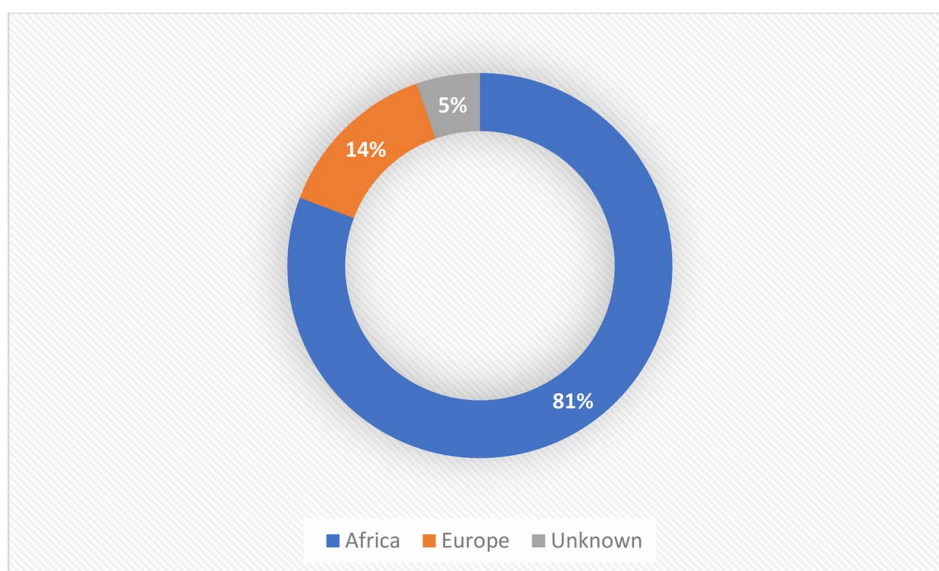


Fig. 2 Distribution of palm oil adulteration cases by region.



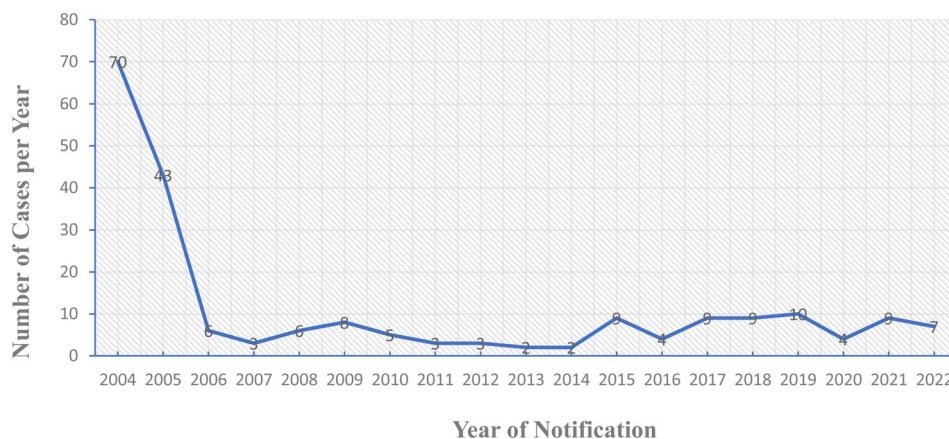


Fig. 3 Number of cases reported per year within the period of 2004 to 2022.

palm oil adulteration from 2004 until 2022. The RASFF report indicates that palm oil adulteration was very high in the years 2004 and 2005. A total of 70 and 43 respectively cases were confirmed, respectively (Fig. 3). Subsequently, there was a drastic decrease in reports of palm oil adulteration between the years 2006 to 2014, with very few cases reported towards the end of 2022 (ranging from 2 to 10 cases). This drop could be due to consumer awareness through public education and an increase in analytical testing. As reported previously, the intentional addition of Sudan dyes into food commodities intensifies and maintains the natural appearance of the oil.<sup>16</sup> The first reports of this type of fraud came after it was discovered in 2003 that chilli products from India were being adulterated with dyes.<sup>17</sup> The earlier notification of Sudan dyes in chilli powder prompted the EU to introduce regulatory legislation requiring regular testing of these dyes in food commodities imported into a Member State.<sup>18</sup> Palm oil was not exempt from this EU legislation and testing of imported food products was conducted. This resulted in a rapid increase in the testing of palm oil between the years 2004 and 2005, when the highest number of reported cases of Sudan dye adulteration of palm oil were recorded. This has not only helped to reduce the adulteration of palm oil with Sudan dyes, but has also made the authorities more aware of fraudulent behaviour and improved the testing of palm oil and other commodities as a preventative measure.

### 3.4 Quantity of Sudan dye present in palm oil

Various levels of Sudan dye ranging from 2 to 1500  $\mu\text{g kg}^{-1}$  were identified in the samples of palm oil from different countries which deal in the production of palm oil as shown in Table 1. Sudan IV dye was identified in almost all countries that export palm oil into Europe, and there were few or no reported cases of Sudan I and II dye, but Sudan III and IV have the highest levels with concentrations in  $\mu\text{g kg}^{-1}$  detected based on the country of origin as shown in Table 1.

### 3.5 Severity and notification basis of palm oil adulterated with Sudan dye

It was observed that from 2004 to 2022, 156 cases of Sudan dye adulteration in palm oil were reported in the RASFF portal and

Table 1 Concentration of Sudan dye types within some countries of origin reported in the RASFF database

Country of origin	Concentration of Sudan dyes $\mu\text{g kg}^{-1}$			
	Sudan I	Sudan II	Sudan III	Sudan IV
Ghana	—	—	241.9	619
	—	—	30	522.9
			—	489.3
				74
				505
Guinea	—	—	1500	—
Cote D'Ivoire	110	2	5	—

classified as undecided in terms of risk detection level. Forty-one (41) of the cases were classified as serious, with two cases classified as not serious (Fig. 4). This classification was made in terms of the health implications posed on consumers after consumption of these adulterated palm oils. The cases of Sudan dye adulterated palm oil reported by the RASFF also indicate the type of notification and the number of cases per type of notification received by regulatory authorities (Fig. 5). These notifications were categorised into border rejection, alert and information for follow-up. The report indicates that palm oil consignments identified as positive for Sudan dye adulteration by the border inspection authorities are denied access within the EU and most consignments are rejected and destroyed by the border inspection authorities. The alert and information categories contain data, mostly gathered by border control teams and officials on the market, to alert and inform regulatory bodies of any suspicion of adulterated oil or fraudulent activities by perpetrators. The results indicated that there was a total of 42 border rejected cases, 74 alert cases and 96 required information for follow-up cases. The RASFF report also confirms that the border rejection cases started from April 2008 until the current day, as compared to the alert and information for follow-up which began earlier in 2004. Despite this, the number of border rejection notifications are higher than both the alert and information for follow-up (and higher than the two combined) between 2008 and 2022. The total number of border



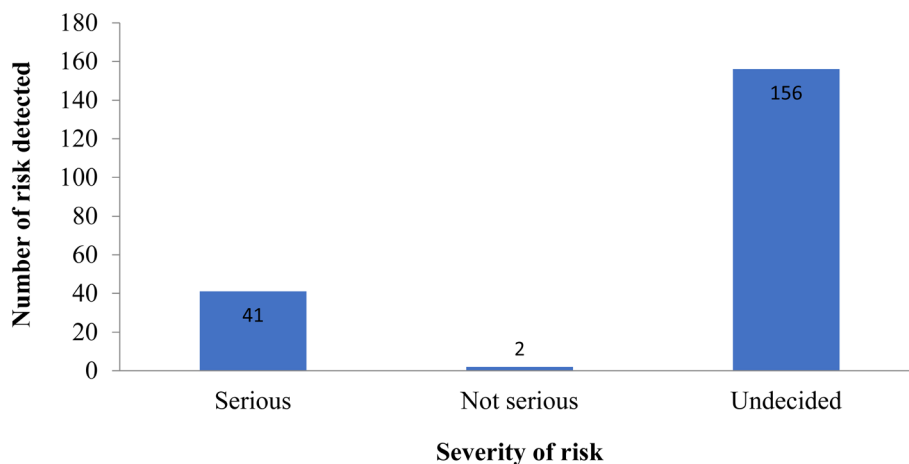


Fig. 4 Severity of palm oil adulterated with Sudan dye between 2004 and 2022.

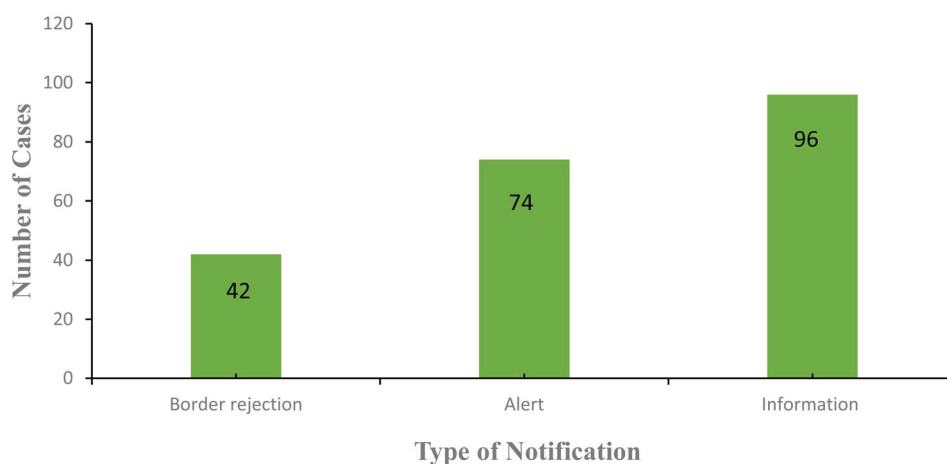


Fig. 5 Types of notifications on palm oil adulteration over 18 years.

rejections, alerts and information for follow-up during this period was 42, 21 and 18, respectively.

#### 4. RASFF discussion

The history of the intentional addition of Sudan dyes in foodstuffs was first raised in 2003 in Indian chilli powder (Haughey *et al.*, 2014). This led to more frequent testing of food commodities to screen for the adulteration of Sudan dyes. This also included the testing of imported palm oil into Europe. The palm oil supply chain over the last 18 years has suffered from these fraudulent acts. This article has reviewed all the Sudan dyes cases in palm oil by country of origin as reported by RASFF between the years 2004 to 2022 and has identified fraudulent reports in the palm oil supply chain, which are attributed to adulteration. In this current study, Ghana recorded the most cases of adulteration of all notifying countries. This is probably due to Ghana being the main African country exporting palm oil to Europe during the early 2000's. Ghana's production of palm oil was approx. 260 000 tonnes in 2019 according to the FAO Report 2022.<sup>19</sup> Nevertheless, Indonesia and Malaysia are dominant in the production of palm

oil with 43 million tonnes and 20 million tonnes, respectively (FAO, 2022) and are the top exporters of crude palm oil in the world.<sup>20</sup> Despite this, these countries have no reported alerts by RASFF regarding any adulteration issues. A study conducted<sup>2</sup> reported that approx. 34% of all palm oil exported to Europe first has to pass through transit countries such as the Netherlands. This study shows that the level of palm oil adulteration being detected varies from country to country.

Sudan IV dye is a category 3 carcinogenic substance that has no tolerable daily intake value and hence is not safe for human consumption. It is mostly used as a dye in the manufacturing of plastics and textiles. Most palm oil adulteration encountered in the current study reported Sudan IV dye as the major adulterant. Although the levels of Sudan I, II and III dyes detected in palm oil were low compared to that of Sudan IV dye, the use of these dyes as food colourants have also been banned in the EU and the USA.<sup>21</sup> To ensure that this ban was effective, between the years 2003 and 2005 the EU required importers of palm oil to include an analytical certificate declaring that the palm oil was free from Sudan I-IV dyes.<sup>22-24</sup> Nevertheless, the number of cases of palm oil adulteration with Sudan dye reported in the



RASFF portal remained very high in 2004 and 2005. This is due to increased testing of imported palm oil, which was performed as a required by the EU Commission. However, the use of illegal dyes still continues to be problematic and notifications are still being reported in the RASFF portal.

Adulteration of palm oil was high in African countries, as reported on the RASFF portal from 2004 to 2020. Crude palm oil is well known in African diets and is one of the most widely used vegetable oils with many nutritional benefits due to its high beta-carotene content.<sup>1</sup> The addition of unauthorised colourants such as Sudan dyes could have detrimental health effects on consumers. European countries have recorded few cases of palm oil adulteration, although they remain the world's second largest importer of palm oil. This may be due to the test certificate required by the EU. Strict measures have also been taken by the EU to ensure that imports of palm oil only come from certified sources.<sup>2</sup> The unknown country of origin reported by the RASFF portal could be attributed to the fact that the names of the countries' did not appear on the label. This is consistent with a study reported by Genualdi *et al.*,<sup>21</sup> where 9 out of 30 or almost a third of all palm oil samples did not have the country of origin stated on the label.

Although several measures have been put in place to ensure the traceability of palm oil within the supply chain, it is still

a challenge for regulators. In this current study, information for follow-up on palm oil adulteration had the highest number of notifications, followed by alert notifications. EU legislation and the testing commission need to have analytical tools in place, which are rapid and portable, to conduct spot checks at processing centres, marketplaces throughout supply chains, to help catch and deter the perpetrators and keep consumers safe.

## 5. Detection techniques of Sudan dye adulteration in palm oil

### 5.1 Chromatographic techniques

Chromatographic techniques are normally used to evaluate palm oil integrity; thus, the presence of Sudan dyes is detected by high-performance liquid chromatography (HPLC), gas chromatography mass spectrometry (GC-MS), gas liquid chromatography (GLC), and chromatography-diode array detection (LC-DAD).<sup>25</sup> These techniques are renowned for producing outcomes that are precise and accurate. However, they have reportedly been shown to have several downsides, such as tedious and time-consuming sample preparation and requirement of technical expertise for new method development. This is a challenge in the face of sustainability and affordability for lower-income countries (Fig. 6).<sup>26</sup>

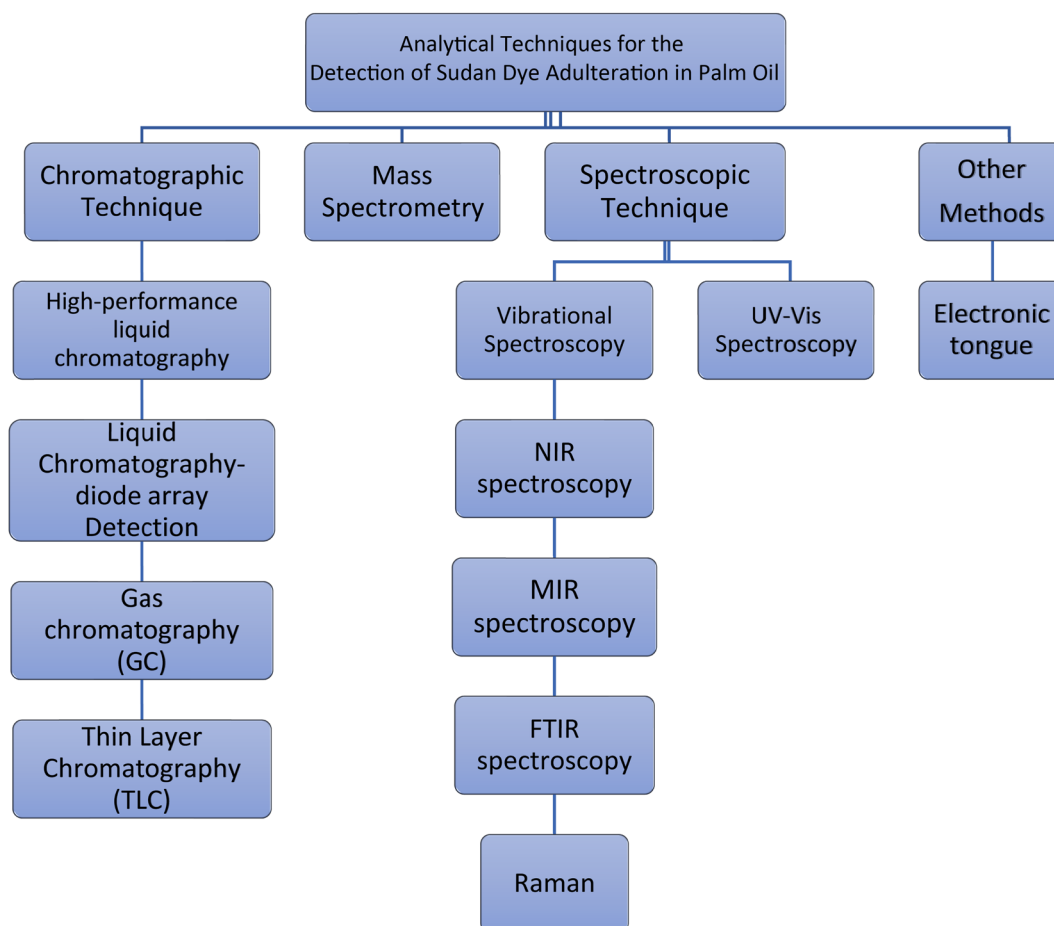


Fig. 6 Analytical techniques for the detection of Sudan dye adulteration in Palm oil.



**5.1.1 High-performance liquid chromatography (HPLC).** The HPLC method of Sudan dye determination in palm oil is a quantitative analysis which has been predominantly used over the last few decades and is known for a high detection level.<sup>9</sup> Sudan dye concentrations between 0.001–2.58 mg L<sup>-1</sup> were detected by the HPLC method.<sup>27</sup> Another research study<sup>28</sup> also reported the level of Sudan dye detection by HPLC showing calibration graphs with correlation factors of 0.9969 and 0.9952 for Sudan I and IV, respectively, in tomato sauce.

**5.1.2 Liquid chromatography-diode array detection (LC-DAD).** A recent study<sup>2</sup> reviewed the detection of Sudan dyes I–IV in palm oil using LC-diode array detection (DAD) analysis. The study looked at the benefits and drawbacks of each approach for spotting tampered samples. To test the procedures, samples that were already known to be free of Sudan I–IV were purposefully spiked with amounts just above the detection threshold. Subsequently, Sudan I–IV was examined in a total of 20 brands of red palm oil samples using LC-DAD. Four of the 20 brands examined had Sudan I–IV levels that could be detected. The limit of detection (LOD) for Sudan dye is 0.25 µg mL<sup>-1</sup> and limit of quantification (LOQ) is 0.50 µg mL<sup>-1</sup>.<sup>29</sup> This method achieves low limits of detection and addressed the drawbacks of other techniques. Also, this method requires simple sample preparation which is an advantage.

**5.1.3 Gas chromatography mass spectrometry (GC-MS).** Sudan dyes can be detected and measured in samples of palm oil using GC-MS. For instance, a study that combined GC-MS with HRMS was able to find Sudan dyes I through IV in tainted palm oil, tomato sauce, and powdered chilli. The approach confirmed the adulteration of four out of the five samples of palm oil supplied by the Food and Drug Authority, with an identification limit of 0.5 to 1 mg kg<sup>-1</sup> for all matrices. Sudan IV was identified in samples of palm oil using GC-MS in combination with surface-enhanced Raman spectroscopy (SERS) and chemometric techniques. Sudan IV was identified using the 1388 cm<sup>-1</sup> Raman peak with a linear range of 0.05 to 5 mg kg<sup>-1</sup>.<sup>30</sup> Therefore, using GC-MS to examine the adulteration of Sudan dyes in palm oil is a valuable technique and offers the best results. It can identify the presence of azo dyes, which are prohibited, and provides quantitative as well as qualitative details on the components of the palm oil samples. Additionally, HRMS or SERS can be used in conjunction with GC-MS to increase the sensitivity and specificity of the analysis.<sup>1</sup>

**5.1.4 Gas liquid chromatography (GLC).** Gas liquid chromatography (GLC) is a technique that can be used to analyse the presence and concentration of Sudan dyes in palm oil. GLC aims to separate mixture components according to how volatile and affluent they are to stationary phases. An inert gas (often helium or nitrogen) transports the vaporised palm oil through a column that has been coated with a liquid or solid stationary phase after being introduced into a heated injector. Depending on how they interact with the stationary phase and the column's temperature, the components of the sample will have various retention durations. A detector, such as a flame ionisation detector (FID) is then used to find the components that have been eluted. GLC has been known to be one of the potential

techniques for analysing Sudan dyes in palm oil.<sup>31</sup> The stationary phase was a capillary column coated with polyethene glycol, and the detector was an FID. Before injection, the Sudan dyes were pre-concentrated and purified from the palm oil matrix using a solid-phase extraction (SPE) technique. They successfully and accurately identified the Sudan dyes (I, II, III, and IV) in samples of palm oil. The researchers discovered that several samples from China contained Sudan dyes at concentrations between 0.21 and 6.15 mg kg<sup>-1</sup>.<sup>1</sup> This technique offers another potential approach for utilising GLC to analyse Sudan dyes in palm oil. GLC has good sensitivity and selectivity, and was able to identify two Sudan dyes (III and IV) in samples of palm oil. It was discovered that certain samples from Africa contained Sudan IV dye at concentrations between 0.05 and 0.15 mg kg<sup>-1</sup>.<sup>1</sup>

**5.1.5 Thin layer chromatography (TLC).** In thin-layer chromatography, a liquid serves as the mobile phase, while an adsorbent solid or liquid is applied thinly on a plate to isolate specific components from a mixture.<sup>32</sup> A review conducted by other authors<sup>33</sup> shows that thin-layer chromatography could not detect Sudan III dye in palm oil at a concentration of 1 mg L<sup>-1</sup> but was able to detect a concentration of 10 mg L<sup>-1</sup> and above for Sudan III dye in palm oil within 10 minutes. The researcher used concentrated sulphuric acid and hydrogen peroxide as bleaching agents during the method of detection. It must be emphasized that although the method is promising in terms of speed of detection, it could be used as a screening method.

**5.1.6 Mass spectrometry.** Mass spectrometry is one of the common methods used today for determining and validating the presence of adulterants in food. It is known to increase the sensitivity and selectivity of the analysis in complex matrices like Sudan dyes by applying the multiple reaction monitoring (MRM) mode for delivering qualitative and quantitative information. Mass spectrometers provide high mass resolving power and faster acquisition rates.<sup>34</sup> Mass spectrometry can identify and measure Sudan dyes in palm oil by ionizing the molecules and separating them based on their mass-to-charge ratios. The resulting ions can be compared with those of reference standards or databases to confirm the identity and concentration of the adulterants.<sup>30</sup>

Mass spectrometry has several advantages over other methods for Sudan dye detection. These merits include high sensitivity, specificity, accuracy, and speed. Some examples of mass spectrometry techniques that have been applied to Sudan dye analysis in palm oil are gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS), and matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF-MS).<sup>35–37</sup> The limits of detection (LODs) and limits of quantification (LOQs) of Sudan III and Sudan IV dyes in edible palm oils using these techniques were 0.1 mg kg<sup>-1</sup> and 0.3 mg kg<sup>-1</sup>, respectively, according to a study by Andoh *et al.*<sup>10</sup>

## 5.2 Spectroscopic techniques

**5.2.1 NIR spectroscopy.** Near-infrared (NIR) spectroscopy is a promising technique for this purpose, as it can provide



information on the chemical composition and physical properties of palm oil samples in a fast and simple way.<sup>26</sup> NIR spectroscopy can also be coupled with multivariate models to classify and quantify the adulteration level of palm oil samples based on their spectral features.<sup>10</sup> The type and concentration of the dye, as well as the spectrum pre-processing and multivariate analysis methods used, all affect the limit of detection (LOD) of near-infrared (NIR) spectroscopy when evaluating crude palm oil adulterated with Sudan dyes.<sup>27</sup> According to a study by Teye *et al.*,<sup>26</sup> employing portable NIR spectroscopy along with MSC and SVM, the LOD for Sudan I, II, III, and IV dyes was 0.01%, 0.02%, 0.03%, and 0.04%, respectively.

FT-NIR spectrometer has a wider range of wavelengths from 900 nm to 2100 nm, and has a spectral resolution of 5 nm. For the FT-NIR experiment, a tungsten halogen external light source was utilised. The spectrometer needed between 7.5 V and 12 V of power to run. An ARCOptix weighed 1.7 kg and the system had a permanently oriented interferometer. The best result for Sudan dye detection in palm oil was obtained using the FT-NIR approach; according to Basri and co-workers<sup>38</sup> the  $R^2$  values achieved for FT-NIR after applying SNV were 0.9997 for calibration and 0.9996 for prediction. In addition, the RMSEC and RMSEP values for calibration and prediction, respectively, were 0.2673 and 0.3386.

**5.2.2 MIR spectroscopy.** Mid-infrared (MIR) spectroscopy is one technique for analysing the Sudan dye adulteration in palm oil. MIR spectroscopy is a method that measures how much light is absorbed by molecules by using the mid-infrared region of the electromagnetic spectrum. MIR spectroscopy can reveal details about a sample's chemical makeup and structure. Sudan dyes can be detected by MIR spectroscopy because they have characteristic absorption bands in the mid-infrared region, such as the C=N and N=N stretching vibrations.<sup>10</sup> Mid-infrared (MIR) spectroscopy is used to analyse the presence of Sudan I, II, III and IV dyes in palm oil samples. The MIR spectra of 20 palm oil samples with different concentrations of Sudan dyes (0.01–10 mg kg<sup>-1</sup>) were measured using a Fourier transform infrared (FTIR) spectrometer. The outcome showed that MIR spectroscopy and chemometrics could successfully distinguish between samples of pure and authentic palm oil as well as between various Sudan dyes. For both the PCA and PLS-DA models, the classification accuracy was greater than 95%. Spectral identifiers for the identification of the MIR spectra also revealed characteristic peaks for each Sudan dye in the region of 900–800 cm<sup>-1</sup>. The author concluded that MIR

spectroscopy is a rapid, simple and non-destructive method for screening Sudan dye adulteration in palm oil. However, MIR spectroscopy alone may not be sufficient to quantify the adulteration level of Sudan dyes in palm oil, as there may be interference from other substances or variations in sample preparation. Therefore, it is advisable to use MIR spectroscopy in combination with other analytical techniques like mass spectrometry (MS), to confirm the results and improve the accuracy. This is because MS can provide more detailed information on the molecular composition and structure of the sample, as well as the identification of unknown compounds.<sup>40</sup>

**5.2.3 Raman spectroscopy.** Raman scattering is a type of spectroscopy that depends on the inelastic scattering of photons by an incoming light source. The method generates a spectrum from an analyte of interest that is produced by its distinct vibrational chemical bonds and offers details on its structure, interactions, or environment.<sup>39</sup> Raman spectroscopy is a powerful technique for the qualitative and quantitative analysis of Sudan dye adulteration in palm oil.<sup>2</sup> Adade *et al.*<sup>40</sup> reports the application of chemometric techniques and surface-enhanced Raman spectroscopy (SERS) to identify and predict the presence of Sudan II and IV in crude palm oil. SERS requires less sample preparation, is a non-destructive, rapid method, has high reproducibility, is user-friendly, requires less time during analysis, is easy to use and is not limited to the location.<sup>40</sup> The authors used silver nanoparticles as SERS substrates and measured the Raman spectra of the samples in the range of 1800 cm<sup>-1</sup> to 800 cm<sup>-1</sup>. The characteristic peaks of Sudan II and Sudan IV were present at 1388 cm<sup>-1</sup> and 1564 cm<sup>-1</sup>, respectively.<sup>41</sup> PLS regression was used to build calibration models for Sudan II and Sudan IV based on the reference and spectral data.<sup>41</sup> The results showed that the models had good accuracy and precision, with a RMSEP of 0.023 mg kg<sup>-1</sup> and 0.026 mg kg<sup>-1</sup> for Sudan II and IV respectively. The models were also validated by applying them to unknown samples and comparing the predicted values with the actual values. The relative errors were within 10% for both dyes, indicating that the models were reliable and robust.<sup>40</sup> They reported that SERS combined with chemometrics is a sensitive, rapid and non-destructive technique for the detection and quantification of Sudan dye adulteration in palm oil.<sup>42</sup>

### 5.3 Electronic tongue

Using electronic tongue (ET) technology, Sudan dye adulteration in crude palm oil (CPO) can be detected with high accuracy

Table 2 Advantages and disadvantages of the method of detection of Sudan dyes

Chromatographic techniques		Spectroscopic techniques	
Advantages	Disadvantages	Advantages	Disadvantages
Precision Accuracy	Tedious and time-consuming sample preparation Requires technical expertise for new method development	High sensitivity Specificity	Limited penetration depth Equipment cost
High separation efficiency		Non-destructive Short time analysis Cost-effective	Limited detection Interference



Table 3 Principles of techniques for Sudan dye analysis in crude palm oil

Adulterants	Principle of the technique	Range of the spectrum $\text{cm}^{-1}$	Chemometrics	Food sample	Limit of detection	References
<b>Chromatography</b>						
Sudan I & IV	HPLC			Palm oil	0.0002.58 $\text{mg L}^{-1}$	27
Sudan I-IV	LC-DAD			Palm oil	0.25 $\mu\text{g mL}^{-1}$	2 and 46
Sudan IV	GC-MS			Palm oil	0.5–1 $\text{mg kg}^{-1}$	30
Sudan I-IV	GLC			Palm oil	0.21 $\text{mg kg}^{-1}$	1
Sudan III	TLC			Palm oil	10 $\text{mg L}^{-1}$	33 and 47
Lard	DSC		SMLR	Palm oil	0.9582	47
<b>Spectroscopy</b>						
Sudan II & IV	MS		MSV	Palm oil	0.27–0.33 ppm	41
Sudan I-IV	NIR		MSV, SVN	Palm oil	1.1–0.04%	26
Sudan I-IV	MIR	900–800	PCA, PLS-DA	Palm oil	0.01–10 $\text{mg kg}^{-1}$	10
	FTRI	900–2100 nm	SVN	Palm oil	0.01% & 1.9–2.24%	10 and 38
Sudan II & IV	SERS	1200–1800	PLS	Palm oil	0.023 $\text{mg kg}^{-1}$	41
<b>Other methods</b>						
	ET			Palm oil	0.5–1.0 ppm	45

and sensitivity. An ET is a device that mimics the human taste system and can measure the chemical composition of liquids. An ET has been used to detect various contaminants and adulterants in food products, such as pesticides, heavy metals, antibiotics and Sudan dyes in CPO samples.<sup>43,44</sup>

According to Andoh *et al.*,<sup>1</sup> an electronic nose can distinguish between genuine and contaminated palm oil samples by evaluating their optical properties, such as refractive index and spectrophotometric transmittance. The authors also mentioned PCA and excess refractive index to improve the precision of the detection. The performance of ET device when compared with HPLC and SERS, which are conventional methods for Sudan dye detection, was satisfactory. An ET could detect Sudan dyes in CPO at concentrations below the EU standards (0.5–1.0 ppm) with high accuracy and sensitivity.<sup>41</sup> An ET also showed advantages over SERS and HPLC in terms of simplicity, cost-effectiveness, and rapidity.<sup>45</sup> Research shows that much work has not been done on the use of an ET in the detection of Sudan dye adulterated palm oil (Tables 2 and 3).

## 6. Conclusion

According to our review, palm oil adulterated with Sudan I-IV dyes was found to occur yearly although the incidence has reduced as reported in the RASFF database within the period 2004–2022. The number of cases reported per year within the last 18 years shows that the majority of the cases of Sudan dye adulteration originated in Africa. Despite the ban on Sudan dye for use in food, the RASFF suggests that Sudan dye appears in food for all the years under review. The various methods used for Sudan dye detection in palm oil reported in the literature included HPLC, LC-DAD, DSC, GC-MS, and GCL. Spectroscopic techniques such as, NIR spectroscopy, FT-NIR spectroscopy, Raman spectroscopy and SERS were also found though their real application is minimal. With regards to the incidence of

palm oil adulteration with Sudan dye, urgent effort is needed to provide onsite detection techniques. This is particularly important as the majority of the palm oil-producing countries are developing countries where laboratory infrastructure is a challenge and if available not well-resourced to provide timely results. Also, these chromatographic techniques have been associated with the following demerits: data analysis and building calibration models are tedious and time-consuming, and thermal degradation can occur due to high laser intensity and adulterants or fluorescence of the sample which interferes with information. Based on the review, it could be concluded that handheld analytical methods of Sudan dye adulteration could be the way forward for onsite detection of adulteration of palm oil in developing countries.

## Data availability

Readers can access the data at <https://webgate.ec.europa.eu/rasff-window/portal/?event=SearchByKeyword&NewSearch=1&Keywords=sudan>.

## Conflicts of interest

There is no conflict of interest regarding the publication of this paper.

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