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Marker Technologies, the Answer to Fuel Adulteration: An Overview

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ABSTRACT

Gasoline and Diesel are major transport fuels in India. Complaints on adulteration of these fuels at the point of sale or during transportation are a severe problem faced by the country. The fuels are often adulterated with cheaper hydrocarbon products or byproducts or waste stream products for monetary benefits. Gasoline is believed to be adulterated with naphtha, natural gas liquids, kerosene, waste solvents, byproducts from petroleum stream, etc. Large volumes of adulterants both indigenous and imported are available in the market. The scale of fuel adulteration has grown into alarming proportions in the past few years. It is essential to control this menace by using modern and advanced technologies.

Marker is a substance that is selectively administered in fuels to detect adulteration. Marker application is the advanced way of countering the menace of adulteration. Different technologies that are based on different methodologies are available globally. Markers are added in to the adulterant or fuel in parts per billion, parts per million or higher quantity. Marker systems based on various technologies are implemented worldwide with complex systems. An overview of different marker technologies available and their use is discussed in this paper.

These technologies are based on different scientific principles like:

Using dyes and Chemicals as Markers

Extraction of Marker

X-Ray Fluorescence
Spectroscopy (UV, IR & Ion Mobility)

Radio Tracers (Isotopes)

Immunoassay Columns based on Bio & Nano Technology

KEY WORDS:

Marker; Adulteration; Detection technology; Dyes; Immuno-Assay; Nano technology

INTRODUCTION:

Fuels like gasoline (Motor Spirit-MS) and diesel (HSD) often gained attention with respect to adulteration. Huge financial incentives on SKO and LPG arising from differential taxes are one of the primary causes of fuel adulteration. It is evident that the price differential of MS, HSD and SKO in conjunction with little or no tax on materials like Industrial solvents and recycled lubricants provides potential opportunity for unscrupulous elements to resort to fuel adulteration. Significant price difference between MS or HSD and adulterants reportedly makes the adulteration a thriving business. Adulteration of MS or HSD with the kerosene and other low value solvents or off-spec products affects the national exchequer and revenues of the oil companies.

A study by the National Council of Applied Economic Research (NCAER) had shown that about 40% of Kerosene intended for household consumption through Public Distribution System (PDS) outlets is diverted in different ways.

This problem exists more or less in the developing countries. In case of developed countries it is in the form of brand abuse. Most developing countries have not yet established a monitoring methodology and system of fines for adulteration of fuel to act as a strong deterrent.

The main factors leading to the practice of adulteration are;

Differential pricing mechanism of fuels and adulterants

Easy availability of adulterants in the market.

Existence of differential tax levels amongst the base fuels, intermediate products, byproducts and adulterants.

Lack of monitoring and consumers areness.

Price sensitive markets

Lack of transparency and regulatory controls in the import/production-supply & marketing chain for intermediates and byproducts.

In the present scenario different techniques are available to counter this menace of diversion/adulteration. One way of attacking the problem is by having a marker system which will detect adulteration in field or in laboratory. Different marker technologies are available and used across the globe depending on the various geopolitical factors amongst other things. One technology may not be the panacea for all the existing problems in different countries.

Marker is a substance that can be dissolved in a fuel or adulterant, to be subsequently identified through physical or chemical tests in the same fuels marked or other fuels adulterated by such marked fuels or adulterants. These markers do not in any way alter the quality or the performance of the fuel in which they are added.

The different factors affecting the choice of technology can be:

Scale and sensitivity of the problem and stake holders affected

Environment dynamics where the problem exists

TYPE OF ADULTERANTS

Ease in implementing the technology in field across the country.

Degree of susceptibility of technology for manipulation by adulterators

Cost of the technology

Different technologies available are reviewed in the present paper, which may be implemented keeping the above factors in consideration.

COLOUR IDENTIFICATION USING DYES AND CHEMICALS:

Employing dyes as marker for detecting adulteration or diversion of fuels is one of the earliest method. Either the fuel or the adulterant is dyed to give visual differentiation in this process. Dyes are also used for coding Branded fuels which are additised to differentiate them from other normal fuels. These dyes do not in any way alter the quality or the performance of the fuel. The fuels are doped with these dyes in percentage or parts per million levels. Different dyes such as Solvent Red #24, Solvent Red #19, Solvent Yellow #14, Solvent Green #3, Solvent Blue #36 etc. have been used worldwide. In India Blue dye is doped in PDS kerosene for monitoring. Similarly certain chemicals like quinizarin, diphenylamine are also used as markers to a limited extent.

Dye addition has not been very successful as ways and means of removal or obscuring of dyes have been reported which is of great concern. Once the dye is removed detection of diversion or adulteration becomes impossible. Thus usage of dyes can be limited to colour identification by coding or tagging and are not effective in controlling or monitoring fuel adulteration.

EXTRACTION OF MARKER:

Extraction of marker is one more technique used for monitoring adulteration/ or diversion. In this technique the adulterant is doped with a Marker which will not give any visual indication of its presence. However, by using certain methods it can be extracted. For example x marker at very low levels (parts per million or parts per trillion) is added in the adulterant. The samples of fuel which are suspected to be adulterated with this marked adulterant are subjected to test. The presence of marker is identified by extracting the same using suitable extracting in the test. The extracting is having the properties to extract the marker from the fuel and give a change in co lour of fuel sample. This extracting is very unique to the marker. Here the marker acts as a lock and the extracting as the key. When they couple with each other they give colour. One of the typical examples in this category is Furfural, which is used as marker for middle distillate fuels. It is extracted by a 10% solution of aniline in acetic acid to exhibit a bluish red co lour.

Though the method is better than dye marking, there are disadvantages such as.

The slightest contamination fuel by residual marker such as furfural that is at times used for refining gives a false positive test.

The molecule (furfural) may be unstable in certain fuels and may not be detectable in such fuels after storage of three to six months.

The middle distillate fuels tend to discolour to a greater extent during storage and such discolouration is likely to be extracted by extractant like aniline acetate.

At very low level of adulteration extraction and detection of marker may not be effective

Marker being largely organic molecule or dye, it is possible for miscreants to ascertain its identity and can resort to dope it outside the system into the fuel to misguide authorities involved in prosecution and monitoring of adulteration. This is of huge importance as prosecution is based on the evidences and results and it can be effective if the technology used is fool proof and the facts are admissible and valid in the court of law.

MARKERS BASED ON ECTROSCOPY

Marker based on molecular spectroscopy techniques involves doping of marker that responds to a specific source of energy into adulterant or fuel and its detection is done with the corresponding spectroscopic technique. Technologies using different spectroscopy techniques are:

X-Ray Fluorescence

Ion Mobility Spectroscopy

Infra Red Spectroscopy

UV Spectroscopy

The implementation and ease of adaptation of these technologies based on the above techniques is largely governed by.

Ease of testing- in field and Operation

Frequency and bulk of testing

Laundering aspect

Detection at lower concentrations (i.e.> 5%)

In environments where detection of adulterant in fuel is less than 5 %, technology based on X-Ray Fluorescence, IR and UV spectroscopy have limitations of detection and thus have not been successful. However, technology based on Ion-Mobility Spectroscopy has gained much of attention in the recent times. Brief description of some of the techniques are as under.

1. FLUORESCENCE: X-RAY

Markers have been developed based on the X-Ray Fluorescence spectroscopy are added in to the adulterant at very low levels and their presence is observed in fuel using X-Ray Fluorescence Spectrophotometer.

The marker molecule in the fuel is exposed to short-wavelength X-rays or Gamma rays. Then ionization of atoms in marker component happens during the exposure involving release of one or more electrons from the atom as it is exposed to radiation with energy greater than its ionization potential. X-rays and Gamma rays exposure can expel tightly-held electrons from inner orbital of the marker atom rendering the electronic structure of the marker atom unstable. After this the electrons in higher orbital tend "fall" into the lower orbital to attain stability. During this process, energy is released in the form of a photon, which is equal to the energy difference of the two orbitals involved. Thus, the material emits energy (radiation), which is specific to marker atoms present. The term fluorescence is a phenomenon in which the absorption of higher-energy radiation by electrons results in the re-emission of energy in the form of radiation while attaining stability. Figure 1 shows the schematic diagram of analysis of fuel samples. Figure 2 shows typical X-Ray Fluorescence spectrophotometer.

Figure 1: Schematic diagram of typical XRF analysis.

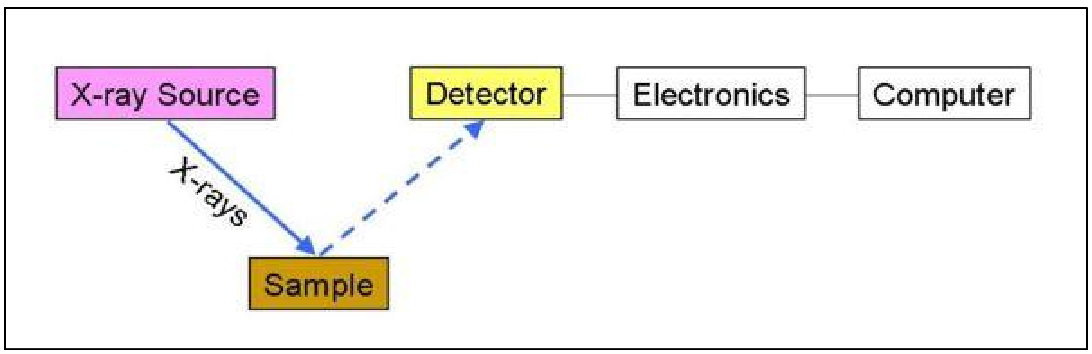

Figure 2: XRF used in field kept in backside of the Multi Utility Vehicle.

Though the technique is effective there are difficulties in testing in the, field because of equipment size which is one of the reasons for its limited use. Since, XRF is expensive the cost of sampling and analysis on site is also very expensive. Moreover it has been established that using this technique detection > 5 % of adulterant in fuel is not consistent which appears to be a concern

2. ION MOBILITY SPECTROSCOPY:

Ion mobility spectroscopy (IMS) is an advanced technique and also known as plasma chromatography, it is a technique that separates ions based on the rate of their movement in an electric field. This technique is similar to the flight mass spectroscopy, except that IMS doesn t involve the use of high vacuum but it operates at near atmospheric pressure. Units working on the IMS technique are widely used as chemical detectors for explosives, chemical agents, monitoring of hazardous substances in atmosphere etc. IMS

Testing by IMS is simple and is done by introducing the sample vapor in the IMS unit. The primary method of introduction is to sniff or draw-in the atmosphere above the sample which is called the headspace. This is done by using a pump, which is inbuilt within the IMS. The pressure in the IMS is typically 0-2 atmosphere. The vapors in the headspace are taken into a chamber by the pump. In the chamber the molecules are ionized by an ionization source. The most common ionization source is nickel 63 which is a radioactive source that ionizes vapor by the emission of low energy beta particles. After the ionization the ions enter a region defined by an electric potential gradient and into a drift area. The drift area contains an electrostatic charge across it. The ions move down through the drift area until they hit a detector. The travel speed of the ions in the drift area is ion specific. The difference in the arrival time of the ions at the detector is used for identifying different types of molecules in the mixture.

This technique is very effective and used in detection by placing IMS on the top of tank lorry or the tank. Markers that can be detected by IMS equipment are already doped into the adulterant. IMS equipment is easy to carry. However, it may not be very cost effective if large numbers of samples are tested simultaneously at various sites. Figure 3 shows typical IMS equipment.

igure 3: A typical IMS detector

Infrared spectroscopy is used when the markers can be detected based on near IR techniques and similarly the UV spectroscopy is used for markers that can respond to UV radiation.

RADIOTRACERS AND ISOTOPES:

Radiotracers and isotopes can also be employed as markers and detected with radiation measurement techniques. However using radio active materials are not socially acceptable. Further usage of special equipment and precautionary measures associated with their handling while obtaining measurements makes it costly and not practicable proposition in the field.

TRACING ADULTERATION USING IMMUNO ASSAY (IAS) COLUMNS:

Monitoring and controlling of diversion or adulteration using Immuno-Assay columns (IAS) is unique technique based on Bio & Nano technology. It works on the concept of antigen-antibody pairing (fig 4). Here the marker which is an antigen is added into the adulterant and is detected by concentrating it on an IAS column. The marker is very specific and will only bond to the antibody present the column. The presence of marker will result in change of the colour specific to marker and antibody. The advantage of the techniquesis:

Performing the test in field   Qualitative nature

Gives results at very low level adulteration (1%adulterant in fuel)

Marker is added in very low concentration (PPT), and thus cannot be removed

Cost effective

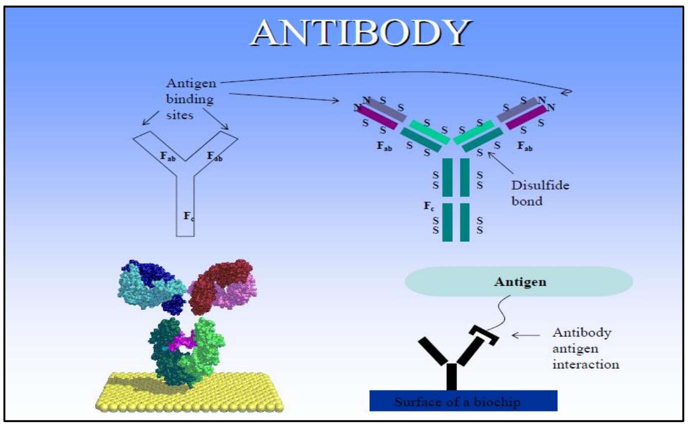

Figure 4: Typical mechanism of Antigen - Antibody Pairing

This technique is presently used in India and other countries on a large scale. In India PDS kerosene is marked and the test is conducted at the retail outlets.

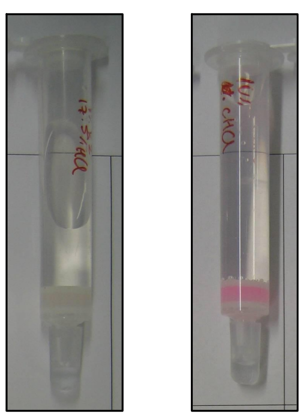

Figure 5: Left - IAS column- blank column and Right IAS column turning pink after test (test performed on fuel adulterated with marked kerosene).

CONCLUSION:

Adulteration of motor fuels is a menace which is causing revenue drain for the developing countries like India. The specifications and test methods currently available for fuels address the fuel performance in the automobiles. Though these tests can be used for finding out fuel adulteration to a limited extent, they can not accurately detect the adulterants at lower levels i.e. when less than 5% adulterants are present in the fuels.

Various other techniques employing markers are available for detecting diversion or adulteration of fuels. However, the use of the right technique for the prevailing environment depends on the severity, scale and extent of the problem, ease of performing the test, economics such as return on investment and accuracy of detection. Based on the information available on the marker based techniques a list of desirable characteristics for using a marker is listed below. These characteristics can be used for initial screening of the markers to fight the menace of adulteration and diversion of fuels.

Characteristics for Evaluation of Markers:
Marker should be unique and easily miscible in the fuel to be marked.

It should be available as a concentrated solution and easily mix in the fuel or adulterant.

Easily detected at low levels by simple qualitative tests in the field conditions (colour etc).

Should not be masked or obscured by unstable and other components of the fuels which are slated for marking or monitoring.

Should be stable over a period equivalent to anticipated storage period of the fuel or adulterant that is being marked.

Should not have any impact on the fuel application and other properties
It should preferably contain components that can not be easily laundered and can also be quantified employing laboratory methods
Should be safe to handle and testing
Cost effective and sustainable over a long period.

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