

# Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in Paraffinic base oil by GC-MS/MS using an efficient extraction method

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### 1. Overview

PAHs belong to a category of typical persistent organic pollutants that are extensively present in environment [1]. These are generally formed due to incomplete combustion of organic matrices such as wood, rubber, coal and oil. One such oil which is often used for various lube and non-lube applications is paraffinic base oil. PAHs can get incorporated during the production process into such diverse matrices and can be present in various amounts in final products. Thus, presence of certain PAHs must be limited to protect human health and environment as these substances can demonstrate strong carcinogenic, teratogenic and mutagenic effects.

This study reports a selective and reliable analytical method for quantitation of PAHs in paraffinic base oil by using GC-MS/MS triple quadrupole system.

# 2. Introduction

Paraffinic base oil is used primarily as a main raw material in various formulations and has found a wide range of industrial, medical, cosmetic and other versatile applications in the modern times [2]. Residual PAH estimation in oil has always been challenging due to complex matrix that may result in instrument contamination and co-extractives. An efficient sample extraction and cleanup method based on modified QuEChERS technique is required to reduce and/or eliminate matrix interference and achieve reproducible results. This study demonstrates a simple, reliable and high throughput sample preparation method for selective estimation of 16 PAHs in paraffinic base oil using GC-MS/MS.

## 3. Materials and methods

The reference standard mixture for 16 PAHs under study was procured from Restek with catalogue number: SV Calibration Mix #5/610 PAH Mix; Catalogue # 31011

The above reference standard was used for Scan identification, followed by calibration and recovery studies. Two paraffinic base oil samples with lighter and heavier paraffinic compositions were procured locally and were used to prepare matrix-matched calibration standards. GCMS-TQ8040 NX (Figure 1), manufactured by Shimadzu Corporation Japan, was used to quantify PAHs in paraffinic oil sample.

### 3-1. Method development

Shimadzu Smart Environmental Database for GC-MS/MS contains 527 compounds with ready to use Multiple Reaction Monitoring (MRM) transitions and optimum Collision Energy (CE) values enabling quick MRM method setup. From this database, 1 target and 3 reference MRMs were selected for 16 PAHs. The chromatography parameters along with Smart Database were used to automatically create final MRM method with optimum time segments. This greatly reduced the time for development and optimization of instrument parameters. Shimadzu's data processing software 'GCMS Solutions Version 4.53' was used for data processing, which helped in evaluating validation parameters with ease. Sample preparation method was developed based on modified QuEChERS and was optimized in order to achieve efficient and consistent recoveries. The method was part validated with parameters such as linearity, LOQ, precision and spiked recovery studies.

#### 3-2. Sample extraction

This study uses extraction procedure in which modified QuEChERS method was adopted.. Initially, 5% w/v sample was extracted with acetonitrile and silica salt. After phase separation, upper acetonitrile layer was subjected to cleanup using C18 and MgSO<sub>4</sub> [3]. Post centrifugation, the upper layer was collected and used for GC-MS/MS analysis as per conditions described in Table 1.

### 3-3. Analytical Conditions



Figure 1. Shimadzu GCMS-TQ8040 NX

Table 1. Instrument configuration and Analytical Conditions: GC-MS/MS

#### **System Configuration**

Instrument	: GCMS-TQ8040 NX
Auto-injector	: AOC-20i + s

Column : SH-I-PAH (60 m × 0.25 mm I.D., df = 0.10 μm) Part No: 227-36074-02

iner : Restek Topaz Liner, Split (with wool)

# Injector temp. : 330 °C

Column oven temp : 180 °C (2 min), 5°C/min to 260 °C (0 min),

15 °C/min to 350 °C (12 min)

#### Run time : 36 r Injection mode : Spli

Injection volume : 2 u Carrier gas : He

Linear Velocity : 40.0 cm/sec (Constant Linear Velocity mode)

#### MS

iterface temp.	: 330 °C
n source temp.	: 230 °C
nization mode	: EI
olvent cut time	: 1.1 min
oop Time	: 0.3 sec

# 4. Results

Validation parameters like linearity, LOQ, precision and recovery were studied.

# 4-1. Linearity

Multi level matrix matched calibration standards were prepared in 2 different matrix blank as per the extraction protocol and injected in GC-MS/MS system. The linearity ranging from 25-100 ppb was plotted for both and results were found to be linear with regression coefficient of determination (r²) more than 0.99. Linearity plot of representative compounds are shown in Figure 2.

Matrix matched standard linearity also showed an accuracy within 80-120 %.

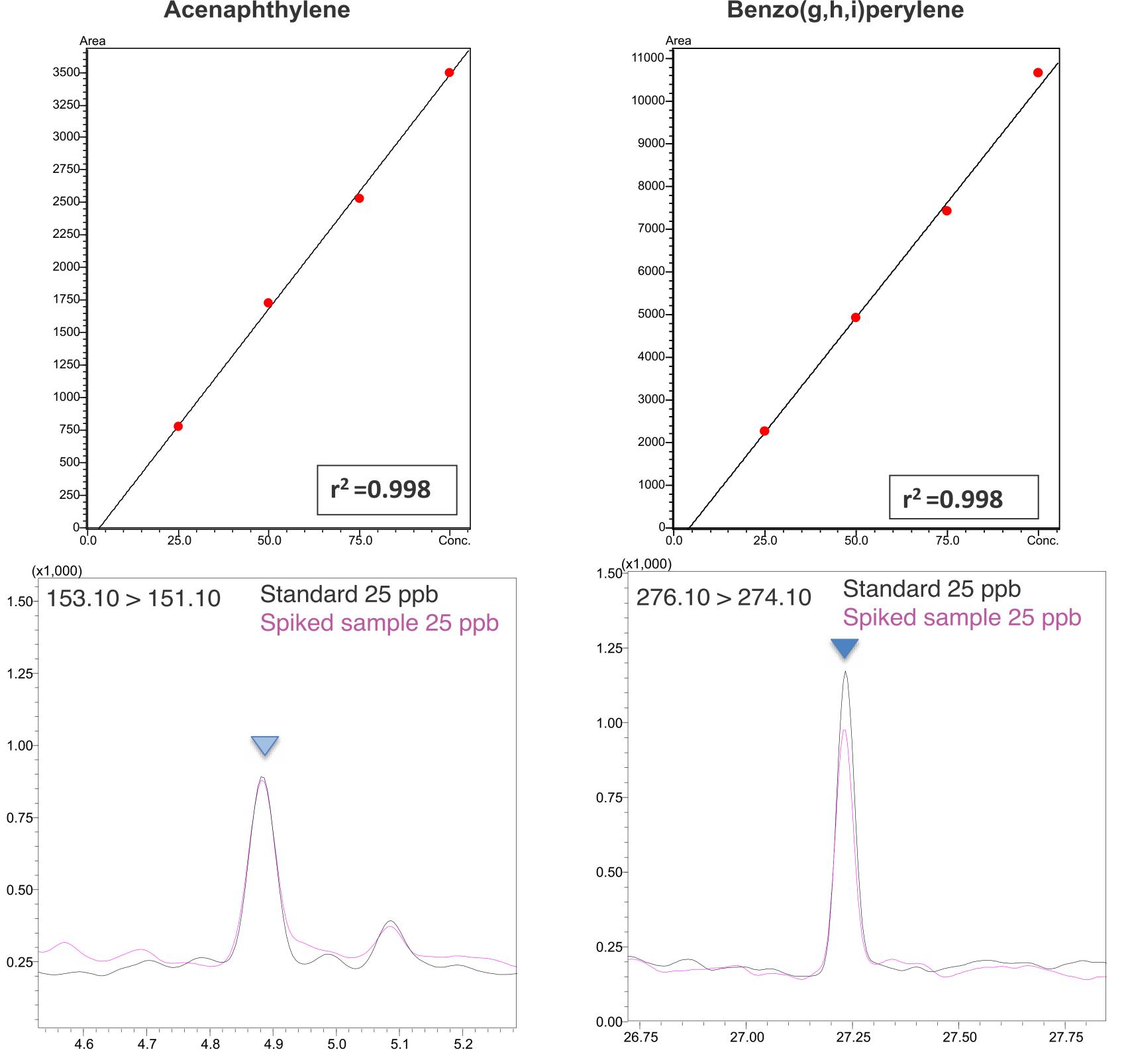


Figure 2. Linearity plot and overlay of matrix matched standard with recovery samples at LOQ level for representative compounds

### 4-2. Limit of Quantitation (LOQ):

LOQ for the 16 PAHs were estimated based on the S/N (ASTM), repeatability & recovery. The LOQ of 25 ppb was achieved for all 16 compounds for both sample matrices.

### 4-3. Precision: Repeatability (RSD<sub>r</sub>)

Repeatability experiment was performed by injecting six replicates at LOQ level (25 ppb) for both the paraffinic base oil samples. All compounds exhibited area precision (% RSD) at LOQ level below 15%. (n=6)

### 4-4. Recovery

Recovery was evaluated by analyzing pre-spiked samples at 25 ppb (six spiked samples each for both the paraffinic oils) against matrix matched calibration linearity samples plotted between 25-100 ppb. Average recovery values for 16 PAHs were found to be within 70-120 %. Overlay of matrix matched standard with recovery samples at LOQ level for representative compounds is shown in Figure 2. Also, area precision (% RSD) for six replicates at spiked LOQ level was below 20%. The plot of %RSD at LOQ level and %recovery at spiked LOQ level for Light fraction oil sample and Heavy fraction oil sample is presented in Figure 3. and Figure 4. respectively.

# 4-5. Sample results

Although in both the samples, most of the PAHs were not detected, in light fraction oil sample, two compounds namely benzo(b)fluoranthene and benzo(k)fluoranthene were present below quantitation limit.

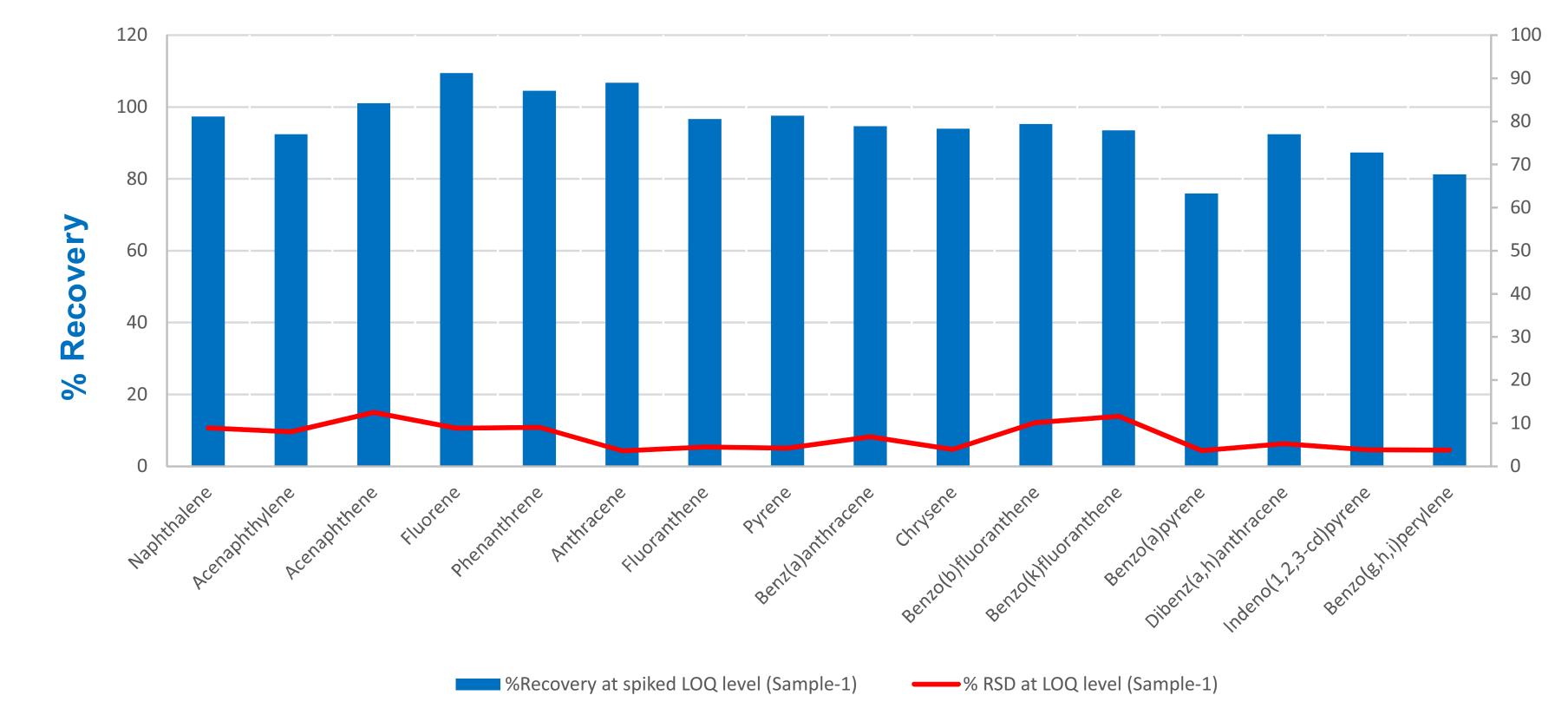


Figure 3. Plot of %RSD at LOQ level and %Recovery at spiked LOQ level (Light fraction oil sample )

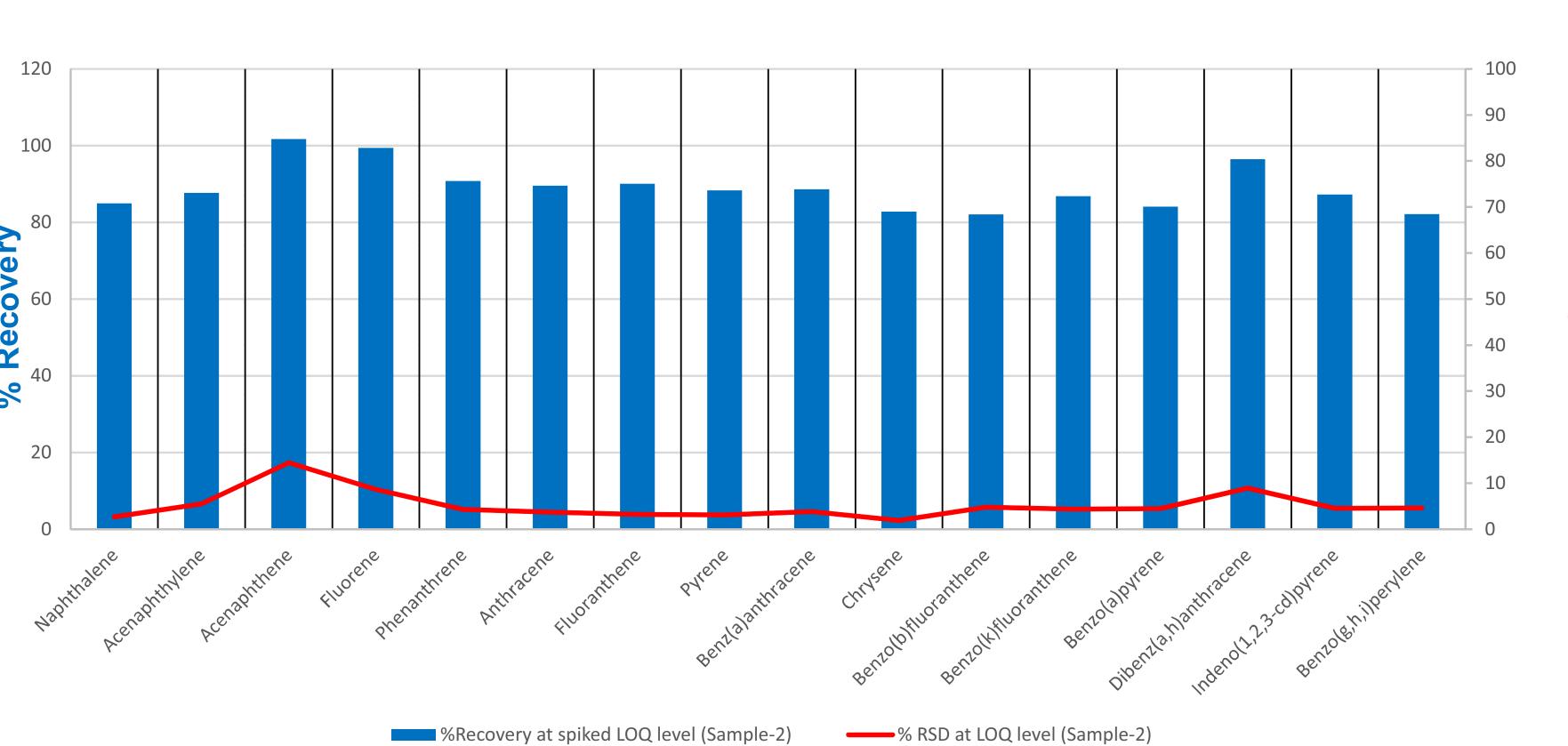


Figure 4. Plot of %RSD at LOQ level and %Recovery at spiked LOQ level (Heavy fraction oil sample)

# 5. Conclusion

- > A simple, reliable and sensitive method has been developed and part validated for determination of 16 PAHs in challenging matrix like paraffinic base oil of different composition
- The method developed on GC-MS/MS proved to be reproducible and efficient as most of the compounds showed good repeatability and recovery at low levels.

# 6. References

- 1. Ifegwu, O. C., & Anyakora, C. Polycyclic aromatic hydrocarbons: part I. Exposure. Advances in clinical chemistry, 72, 277-304, 2015.
- 2. Determination of content of Benzo(a)pyrene and selected Polycyclic aromatic hydrocarbons in extender oil- Procedure using LC cleaning and GCMS analysis. BSI standards publication. BS EN 16143:2013
- 3. Shimadzu Food Safety Booklet: Complete Compilation of Applications for Food Analysis

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