
A REPORT ON
**XRF, FTIR AND GAS PYCNOMETER SPECTROSCOPY
ANALYSIS**
SUBMITTED TO
**CSIR-NATIONAL METALLURGICAL LABORATORY,
MADRAS CENTRE**
(COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH)
CHENNAI, INDIA



SUBMITTED BY
VISU G - 40910012
M.Sc. Chemistry (II year)
SATHYABAMA INSTITUTE OF SCIENCE
AND TECHNOLOGY
SEMMANCHERI, CHENNAI-600119



सी.एस.आई.आर राष्ट्रीय धातुकर्म प्रयोगशाला
मद्रास केन्द्र, वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद
सी.एस.आई.आर, मद्रास कॉम्प्लेक्स, तारमणी, चेन्नै - 600 113
CSIR - National Metallurgical Laboratory Madras Centre
Council of Scientific and Industrial Research, Govt. of India,
CSIR Madras Complex, Taramani, Chennai - 600 113. INDIA.



INTERNSHIP CERTIFICATE

CHENNAI

07/01/2022

This is to certify that **Mr. Visu. G** (Register No. **40910012**) pursuing his **II Year M.Sc. Chemistry** in the Department of Chemistry, Sathyabama Institute of Science and Technology (Deemed to be University), Chennai- 600119, has carried out his internship at **CSIR-National Metallurgical Laboratory, Madras Centre** under the guidance of Dr. T. V. Vijaya Kumar, Scientist In-Charge and Ms. N. Vasumathi, Principal Scientist, CSIR-NML, Madras Centre, Taramani, Chennai from 5th October 2021 to 7th January 2022 as a partial fulfillment of his degree.

T. V. Vijaya Kumar

Dr. T. V. Vijaya Kumar

Scientist In-Charge



N. Vasumathi

Ms. N. Vasumathi

Principal Scientist

Telephone : 044 2254 2077, 22542529, 22542523
Website : www.csircmc.res.in

Working Hours : Monday to Friday
(9.00 a.m to 5.30 p.m)

Fax : 044 2254 1027
E-mail : nmlmc@csircmc.res.in

Head Office : CSIR - National Metallurgical Laboratory, Jamshedpur - 831 007.

ENTS

As a part of my study in B.sc Chemistry course and on my own interest, I was given the opportunity to undertake my internship at CSIR-National Metallurgical Laboratory (NML), Madras Centre, Taramani, Chennai. All the work I have done and the knowledge I have gained so far would not have been possible without the support and encouragement by following, whom I wish to thank. I would like to acknowledge The Chemistry Department Sathyabama institute of science and technology, Chennai for providing me permission to carry out my internship work.

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COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

(CSIR) INDIA



The Council of Scientific and Industrial Research (abbreviated as CSIR) was established by the Government of India in 1942. CSIR is an autonomous body that has emerged as the largest research and development organisation in India with head quarter at New Delhi and a network of 37 national laboratories spread over the country with 39 outreach centres and 5 units. CSIR's R&D expertise and experience is embodied in about 4600 active scientists supported by about 8000 scientific and technical personnel. Although it is mainly funded by the Ministry of Science and Technology, it operates as an autonomous body through the Societies Registration Act, 1860.

The research and development activities of CSIR include aerospace engineering, structural engineering, ocean sciences, life sciences, metallurgy, chemicals, mining, food, petroleum, leather, fuel and environmental science.

CSIR is ranked at 84th among 4851 institutions worldwide and is the only Indian organization among the top 100 global institutions. According to the Scimago Institutions Ranking World Report 2014, CSIR holds the 17th rank in Asia and leads the country at the first position.

The different laboratories & units of CSIR all over India are 44 and I have to mention some research centres:

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1. [Central Electrochemical Research Institute, Karaikudi](#)
 2. [Central Electronics Engineering Research Institute, Pilani](#)
 3. [Central Food Technological Research Institute, Mysore](#)
 4. [Central Glass Ceramic Research Institute, Kolkata](#)
 5. [Central Institute of Mining and Fuel Research, Dhanbad](#)
 6. [Central Leather Research Institute, Chennai](#)
 7. [Central Mechanical Engineering Research Institute, Durgapur](#)
 8. [Central Road Research Institute, New Delhi](#)
 9. [Central Salt Marine Chemicals Research Institute, Bhavnagar](#)
 10. [CSIR Fourth Paradigm Institute, Bengaluru](#)
 11. [Institute of Genomics and Integrative Biology, Delhi](#)
 12. [Indian Institute of Chemical Biology, Kolkata](#)
 13. [Indian Institute of Chemical Technology, Hyderabad](#)
 14. [Indian Institute of Integrative Medicine \(IIIM\), Jammu](#)
 15. [Indian Institute of Toxicology Research, Lucknow](#)
 16. [Institute of Minerals and Materials Technology\(IMMT\), Bhubaneswar](#)
 17. [Institute of Microbial Technology, Chandigarh](#)
 18. [National Aerospace Laboratories, Bengaluru](#)
 19. [National Geophysical Research Institute, Hyderabad](#)
 20. [National Institute For Interdisciplinary Science and Technology, Thiruvananthapuram](#)
 21. [National Institute of Oceanography, Goa](#)
 22. [National Institute of Science Communication And Information Resources, New Delhi](#)
 23. [National Institute of Science, Technology And Development Studies, New Delhi](#)
 24. [National Metallurgical Laboratory, Jamshedpur](#)
 25. [National Physical Laboratory, New Delhi](#)
 26. [Structural Engineering Research Centre, Chennai](#)
 27. [CSIR-UNIT : Open Source Drug Discovery \(OSDD\), New Delhi](#)
 28. [CSIR-UNIT : Traditional Knowledge Digital Library \(TKDL\), New Delhi](#)
 29. [CSIR-UNIT : Translational Research and Innovative Science Through Ayurveda \(TRISUTRA\), New Delhi](#)

30. CSIR Madras Complex (CMC), Chennai

In order to foster multidisciplinary research and to cater to the requirements of the southern region, five major laboratories established regional centres at Madras (Chennai, Tamil Nadu) in a single campus which is known as CSIR MADRAS COMPLEX (CMC). The Five Laboratories having regional centres in the Madras Complex are:

National Metallurgical Laboratory (NML), Jamshedpur.

Central Electrochemical Research Institute (CECRI), Karaikudi.

Central Electronics Engineering Research Institute (CEERI), Pilani.

Central Scientific Instruments Organisation (CSIO), Chandigarh.

National Environmental Engineering Research Institute (NEERI), Nagpur.

1. X-RAY FLUORESCENCE SPECTROSCOPY (XRF)

PRINCIPLE

The effect of X-ray fluorescence is based on the excitation of atoms in the sample. A primary X-ray, typically generated in an X-ray tube, hits an inner shell electron of the atom and ejects the electron from the atom. The open position is filled by an electron from a further outer shell and fluorescence radiation is emitted. The fluorescence energy is equal to the energy difference between the two electron shells. Therefore, the energy of this radiation is characteristic for the atom and indicates, what atom is present in the sample.

SUMMARY

X-ray fluorescence technology (XRF) provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials. It is non-destructive and reliable, requires no, or very little, sample preparation and is suitable for solid, liquid and powdered samples. Depending on the analyzer the covered element range starts with carbon (6) for a qualitative analysis and starts with fluorine (9) for a quantitative analysis. The highest atomic number element, which is covered, is americium (95).

XRF provides detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously.

SPECTRO is a world leader in the manufacture of energy dispersive X-ray fluorescence spectrometers. In recent years, SPECTRO has set standards by further developing X-ray fluorescence technology to create many new fields of operation for ED-XRF spectrometers.

The company offers a complete range of X-ray fluorescence portable spectrometers such as the small handheld XRF, xSORT and the SPECTROSCOUT, a portable spectrometer that brings lab-grade analysis into the field. SPECTRO also brings to market a broad range of bench-top ED-XRF spectrometers for special elemental analysis tasks to multi-purpose laboratory spectrometers for trace element analysis, and a wide range of on-line solutions – whatever your specifications, we can meet them.



APPLICATIONS

- Metallurgy and chemical industry: quantity control of raw materials, production processes and final products
- Paint industry: analysis of lead-based paints
- Fuel industry: monitoring the amount of contaminants in fuels
- Food chemistry: determination of toxic metals in foodstuffs

CONCLUSIONS

Selected examples show the usefulness of HD XRF in a wide range of applications in science, medicine, and industry. By judicious choice of the source, optics, and detector type, and configuration, it is possible to reach previously unattained levels of sensitivity (down to a few

ppb), elemental specificity, and spatial definition in compact, low-power, reliable, rugged, and nondestructive analyzers for clinical-, field-, online-, and laboratory-based applications.



12/17/2021

Sample Name	A1 (2)	Dilution Material	HWC
Method	IRON ORE -test(1)	Sample Mass	5.0000
Sample Folder	December 2021	Dilution Mass	1.0000
Sample Type	Pressed Tablet	Dilution Factor	0.8333
Sample Status	A X A X X X X	Measurement Date	12/17/2021 1:07 PM
Operator	Admin User	Evaluation Date	12/17/2021 1:07 PM

Results - A1 (2)

The error is the statistical error with 1 sigma confidence interval

Element	Concentration	Abs. Error
11 Na ₂ O Sodiumoxide	0.1755 %	0.0013
12 MgO Magnesiumoxide	< 0.0017 %	-
13 Al ₂ O ₃ Aluminumoxide	0.3028 %	0.0023
13 Al Aluminium	0.1602 %	0.0012
14 SiO ₂ Siliconoxide	0.4843 %	0.0022
14 Si Silicon	0.2264 %	0.0010
15 P ₂ O ₅ Phosphorusoxide	1.362 %	0.002
15 P Phosphorus	0.5946 %	0.0009
16 SO ₃ Sulfideoxide	1.120 %	0.002
16 S Sulfur	0.4487 %	0.0007
17 Cl Chlorine	0.1212 %	0.0001
19 K ₂ O Potassiumoxide	0.04171 %	0.00040
20 CaO Calciumoxide	0.8069 %	0.0013
22 Ti Titanium	0.01308 %	0.00023
22 TiO ₂ Titaniumoxide	0.02183 %	0.00039
23 V ₂ O ₅ Vanadiumoxide	-	-
24 Cr ₂ O ₃ Cromiumoxide	0.01152 %	0.00005
25 Mn Manganese	< 0.00002 %	-
25 MnO Manganeseoxide	< 0.00003 %	-
26 Fe ₂ O ₃ Ironoxide	8.823 %	0.007
26 Fe Iron	6.171 %	0.005
27 Co ₃ O ₄ Co3O4	-	-
28 NiO NiO	-	-
29 CuO CuO	-	-
30 ZnO Zincoxide	-	-
33 As ₂ O ₃ As2O3	-	-
56 Ba Barium	-	-
56 BaSO ₄ Barium Sulphate	-	-
57 La ₂ O ₃ La2O3	-	-
58 CeO ₂ CeO2	-	-
82 PbO PbO	-	-

2. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

PRINCIPLE

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture and for the analysis of solids, liquids, and gases. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a development in the manner in which the data is collected and converted from an interference pattern to a spectrum. It is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.

SUMMARY

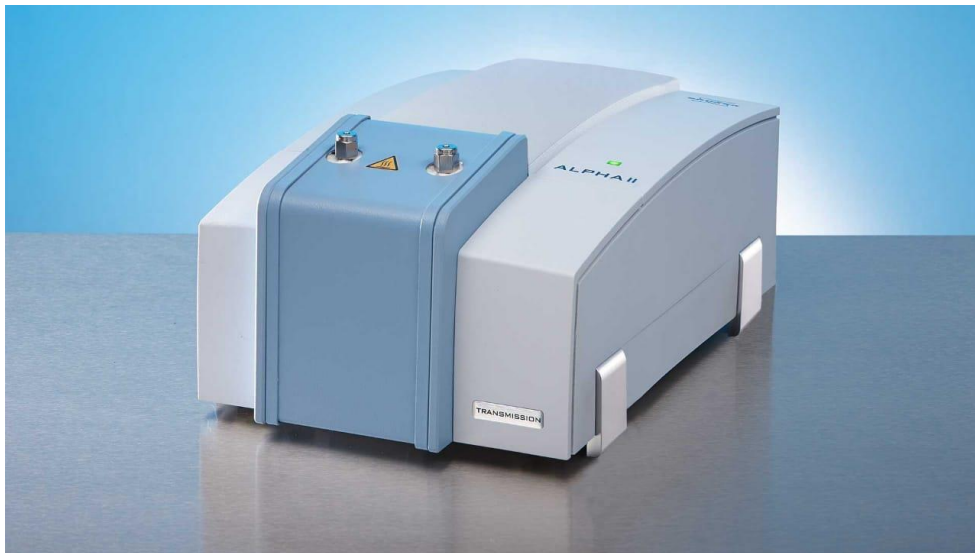
The FTIR instrument sends infrared radiation of about 10,000 to 100 cm^{-1} through a sample, with some radiation absorbed and some passed through. The absorbed radiation is converted into rotational and/or vibrational energy by the sample molecules. The resulting signal at the detector presents as a spectrum, typically from 4000 cm^{-1} to 400 cm^{-1} , representing a molecular fingerprint of the sample. Each molecule or chemical structure will produce a unique spectral fingerprint, making FTIR analysis a great tool for chemical identification.

FTIR spectroscopy is an established technique for quality control when evaluating industrially manufactured material, and can often serve as the first step in the material analysis process. A change in the characteristic pattern of absorption bands clearly indicates a change in the composition of the material or the presence of contamination. If problems with the product are identified by visual inspection, the origin is typically determined by FTIR microanalysis. This technique is useful for analyzing the chemical composition of smaller particles, typically 10 -50 microns, as well as larger areas on the surface.

FTIR analysis is used to:

- Identify and characterize unknown materials (e.g., films, solids, powders, or liquids)
- Identify contamination on or in a material (e.g., particles, fibers, powders, or liquids)
- Identify additives after extraction from a polymer matrix
- Identify oxidation, decomposition, or uncured monomers in failure analysis investigations

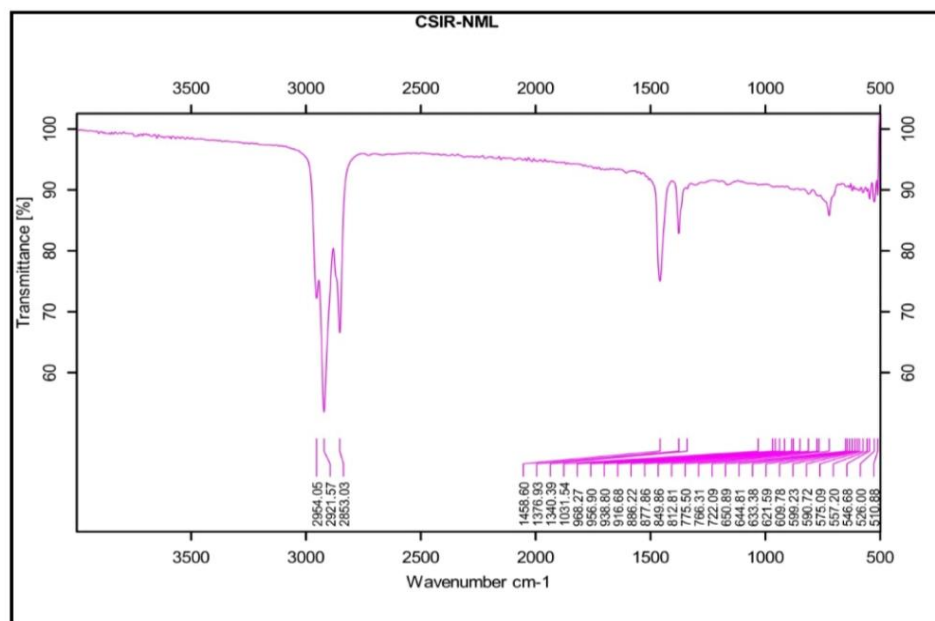
ALPHA II FTIR WITH PLATINUM ATR MODULE





APPLICATIONS

- Food analysis: additives, preservatives, colorants
- Environmental analysis: water, atmospheric particles, gases
- Conservation and restoration of heritage: paintings, sculptures, ceramics, fossils, ivories
- Forensic science: paints, textiles, cosmetics,
- Semiconductor analysis
- Pharmaceuticals
- Physiological samples: malignant cells, bones, hairs
- Multilayer compounds: polymers, paintings, films
- Geological samples: inclusions in stones



FTIR Spectrum of the Diesel Oil.

CONCLUSION

FTIR spectroscopy is a simple, rapid, less expensive and highly sensitive tool for identification as well as differentiation between different genera and species of yeasts.

GAS PYCNOMETER

A gas pycnometer is a laboratory device used for measuring the density, more accurately the volume of solids, be they regularly shaped, porous or non-porous, monolithic, powdered, granular employing the method of gas displacement and the volume-pressure relationship known as Boyle's Law. A gas pycnometer is also sometimes referred to as a helium pycnometer.

TYPES OF GAS PYCNOMETER

The different types of gas pycnometer are:

- Gas expansion pycnometer system

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- Variable volume pycnometer system
 - Gas displacement pycnometer system

GAS EXPANSION PYCNOMETER SYSTEM

Gas expansion pycnometer is also known as constant volume gas pycnometer. The simplest type of gas pycnometer (due to its relative lack of moving parts) consists of two chambers, one (with a removable gas-tight lid) to hold the sample and a second chamber of fixed, known (via calibration) internal volume referred to as the reference volume or added volume. The device additionally comprises a valve to admit a gas under pressure to one of the chambers, a pressure measuring device usually a transducer connected to the first chamber, a valved pathway connecting the two chambers and a valved vent from the second of the chambers. In practice, the sample may occupy either chamber, that is gas pycnometers can be constructed such that the sample chamber is pressurized first or such that it is the reference chamber that starts at the higher pressure. The working equation of a gas pycnometer wherein the sample chamber is pressurized first is as follows:

$$V_s = V_c + \frac{V_r}{1 - \frac{P_1}{P_2}}$$

Where,

V_s is the sample volume,

V_c is the volume of the empty sample chamber (known from a prior calibration step),

V_r is the volume of the reference volume (again known from a prior calibration step),

P_1 is the first pressure (i.e. in the sample chamber only) and P_2 is the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber.

VARIABLE VOLUME PYCNOMETER SYSTEM

Variable volume pycnometer (or gas comparison pycnometer) consists of either a single or two variable volume chambers. The sample cell volume can be at different types and size, like G-DenPyc 2900 technology specified, the volume can be 0.1ml up to 500ml. The volume of the chamber(s) can be varied by either a fixed amount by a simple mechanical piston of fixed travel, or continuously and gradually by means of a graduated piston. Resulting changes in pressure can be read by means of a transducer, or nullified by adjustment of a third ancillary, graduated variable-volume chamber. This type of pycnometer is commercially obsolete; in 2006 ASTM withdrew its standard test method D2856 for the open-cell content of rigid cellular plastics by the air pycnometer, which relied upon the use of a variable volume pycnometer, and was replaced by test method D6226 which describes a gas expansion pycnometer.

GAS DISPLACEMENT PYCNOMETER SYSTEM

INTRODUCTION

Gas pycnometer is recognized as one of the most reliable techniques for obtaining true, absolute, skeletal and apparent volume and density. This technique is non-destructive as it uses the gas displacement method to measure volume. Inert gases, such as helium or nitrogen are used as the displacement medium. Density calculations using the gas displacement method are much more accurate and reproducible than the traditional Archimede's water displacement method.

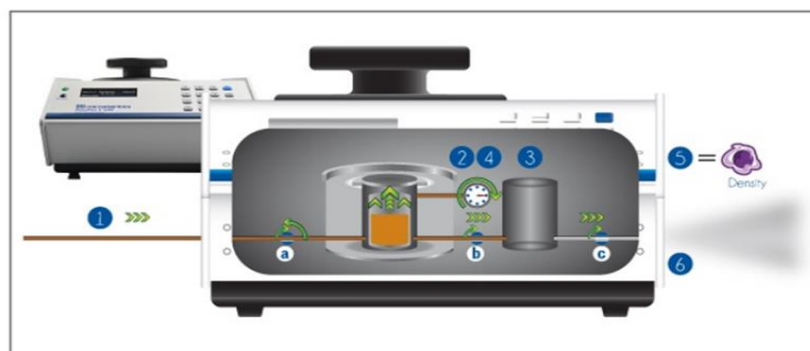
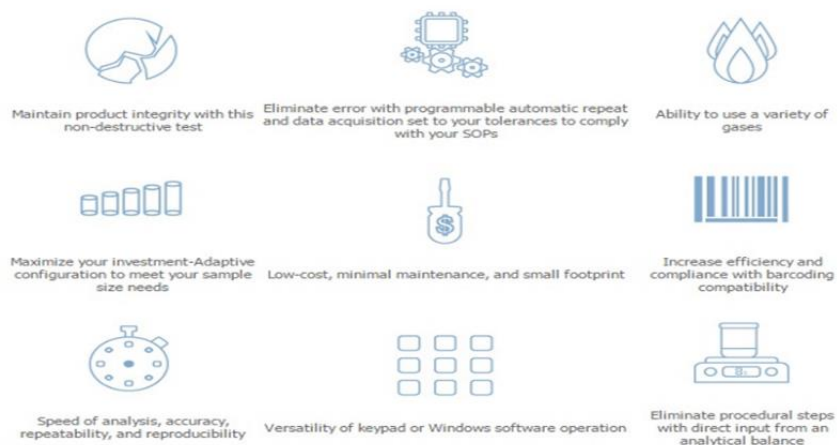
The AccuPyc II 1340 Series Pycnometer (Make: Micromeritics, USA) used for characterisation of concrete raw materials in this work (Fig.6). The equipment is fully automatic pycnometer that provide high-speed, high-precision volume measurements and true density calculations on a wide variety of powders, solids, and slurries based on the weight input of the sample provided. The instrument completes most sample analyses in less than three minutes without sacrificing accuracy. After analyses are started with a few keystrokes, data are collected, calculations are performed and results displayed. A minimal amount of operator attention is required.



Fig.6: Gas Pycnometer (AccuPyc II 1340)

PRINCIPLE OF OPERATION

This technique uses the gas displacement method to measure volume accurately. Inert gases, such as helium or nitrogen are used as the displacement medium. The sample is sealed in the instrument compartment of known volume, the appropriate inert gas is admitted and then expanded into another precision internal volume. The pressures observed upon filling the sample chamber and then discharging it into a second empty chamber allow computation of the sample solid phase volume. Helium molecules rapidly fill pores as small as one angstrom in diameter, only the solid phase of the sample displaces the gas. Dividing this volume into the sample weight gives the gas displacement density.



- | | |
|--|--|
| 1 Inert gas flows into a sample chamber - valve a opens then closes | 4 Equilibrium is reached yet again |
| 2 Equilibrium is reached | 5 Volume divided into sample weight determines density |
| 3 Gas flows into second chamber for volume measurement - valve b opens | 6 Pressure vented off to atmosphere - valve c opens |

APPLICATIONS

Gas pycnometer is used to find density & specific gravity for characterizing a wide variety of solids such as heterogeneous catalysts, carbons, metal powders, soils, ceramics, active pharmaceutical ingredients (API's) and excipients, petroleum coke, cement and other construction materials, cenospheres/glass micro balloons and solid foams

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