Multielement Determination in Gum Opium by Microwave Digestion and Inductively Coupled Plasma Optical Emission Spectroscopy

ᵃR. K. SARIN*, ᵃS. SRIVASTAVA, ᵃA. K. SRIVASTAVA, ᵇG. ANIL, and ᵇM. R. P. REDDY

ᵃ*Central Forensic Science Laboratory, BPR&D, MHA, GOI, Ramanthapur,*
Hyderabad-500 013, India

ᵇ*Centre for Materials for Electronics Technology,*
IDA, Phase-II, HCL Post, Cherlapalli, Hyderabad-500 051, India
e-mail: sarinrk2000@yahoo.com

Inductively Coupled Plasma—Optical Emission Spectroscopy (ICP-OES) was used for multielement analysis in Indian gum opium. All elements including rare earths were scanned using image software and only 13 elements were found to be in quantifiable levels (Ca, Fe, Mg, Al, Si, Mn, Zn, Ni, Cu, Ti, Co, Sr, and Ba). The sample was dissolved completely in closed microwave digestion system using only nitric acid. The ICP-OES/microwave digestion method was found to be fast, accurate, and reliable. The present study was undertaken for the development of multielement determination method for gum opium samples, for screening a large set of samples and creating of a database of elements in Indian gum opium to be used for geographical source correspondence. In order to evaluate the accuracy of the developed analytical method, a recovery study was also undertaken and the recovery was found to be in the range of 97—103 % except silicon where the recovery was in the range of 85—86 %.

Gum opium is an air-dried latex obtained from a plant *Papaver somniferum* L. Opium is a controlled narcotic substance of medicinal and legal importance. It is cultivated in various parts of the world. India is the main [1] opium-producing country. In order to check opium trafficking, law-enforcement agencies need information regarding geographical origin on seized samples of opium. Some of the physical and chemical properties [2] used for opium characterization are general appearance, organic constituents, and inorganic constituents. Mineral characteristic of the plant from region to region depends upon varied concentration of various elements present in it. Major inorganic constituents in opium have been reported using visual colorimetry [3], flame photometry [4], and emission spectrographic techniques [4—8]. The above-referred techniques are tedious and require lengthy sample preparation procedures like ashing and open wet hot-plate digestion. Hence, they are suffering from one or the other limitations like time consuming, less reproducibility, and less number of elements analyzed. Thus, it was necessary to develop a multielement analytical method which is precise and accurate even for volatile elements and which can be used for screening a large number of samples in order to create database of element profile of opium to be used by law-enforcement agencies for source correspondence. Microwave digestion/ICP-OES technique has been employed for the determinations of several elements in botanical samples [9]. But literature reveals that so far no work has been done for the application of the above technique in opium samples. Hence, microwave/ICP-OES technique has been employed to develop a suitable methodology to be used for creating database of inorganic profile of Indian opium. This paper describes quantitative determination of elements present in opium samples.

EXPERIMENTAL

The nitric acid used was of supra pure grade (Merck, Germany). The single and multielement standard solutions used throughout the analysis were procured from Merck, Germany. The deionized water used was prepared using the Nanopure system (Barnstead, USA). Unprocessed Indian gum opium sample obtained from the Government Opium and Alkaloid Works, Government of India, Neemuch, Madhya Pradesh, India was used for this study. Sample digestion was performed using a microwave di-

*The author to whom the correspondence should be addressed.

Table 1. ICP-OES Instrumental Operating Conditions

Sequential spectrometer	Job Yvon JY-24R, 0.64 m Czerny—Turner
Grating	holographic, 3600 grooves/mm
Spectral range	160—500 nm
Slit width	20 nm for entrance and exits, adjustable
HDD Detector	dynamic range 2.5×10^{10}
Image	measures complete emission spectrum in 2 min (230,000 points)
Plasma torch assembly	fused quartz with capillary injection
Nebulizer and spray chamber	cross-flow type nebulizer and Teflon® dual tube spray chamber
Argon coolant gas flow rate	1.5 dm³ min⁻¹
Argon coolant gas flow rate	12 dm³ min⁻¹

Table 2. Operating Conditions of Microwave Digestion System

Frequency	2450 MHz (equivalent to a wavelength of 12.25 cm)
Power supply	220 V/50 Hz, 2.2 kW
Exhaust flow	5 m³ min⁻¹

Digestion Program		
Step No.	Power/W	Time/min
1	400	1
2	0	5
3	250	3
4	0	5
5	500	3
6	0	5
7	650	5

gestion system (MDS) (Model MLS 1200, Milestone, Italy). The instrument used for the determination of major elements in Indian gum opium was an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Model JY-24R, Jobin Yvon, France). A cross-flow type nebulizer was used for pneumatic nebulization in the ICP-OES instrument. The instrumental parameter of the ICP-OES and the microwave digestion system are given in Tables 1 and 2, respectively. The wavelength selected for each element to be determined is listed in Table 3.

Sample Preparation and Procedure

Gum opium samples were dried at 70 °C and powdered with a Teflon rod in a Teflon vessel. A small portion of powdered opium samples was dried to constant mass at 105 °C. About 0.500 g of accurately weighed gum opium sample was transferred into a tetrafluoromethaxil (TFM) vessel and 5 cm³ of water and 10 cm³ of nitric acid were added into the digestion vessel. Seven different sequential steps of microwave heating with varying power and time were applied in order to control the reaction of the sample during dissolution (Table 2). After completing the digestion, the solution was made up to 25 cm³ with nanopure water and analyzed by ICP-OES.

RESULTS AND DISCUSSION

The digestion was carried out using only nitric acid so as to decompose all organic matter into CO_2. Due to the sudden increase in the pressure in organic decomposition a cooling step was alternated between every microwave digestion step. This program was very

Table 3. The Analytical Results of the Sample Dissolved by Microwave Digestion for Recovery Study

No.	Element and wavelength	Results* ρ(found)	Detection limit in	Recovery*/%	
	nm	μg/cm³	ng/cm³	5 μg/cm³ spiked	10 μg/cm³ spiked
1	Ca 317.933	32.55 ± 0.40	24.0	102.29 ± 1.20	101.02 ± 1.29
2	Fe 238.204	5.87 ± 0.15	9.0	101.25 ± 1.15	98.20 ± 1.33
3	Mg 279.553	8.60 ± 0.11	1.3	97.32 ± 0.98	103.54 ± 2.10
4	Si 251.611	6.90 ± 0.18	60.0	86.21 ± 2.40	85.48 ± 3.01
5	Al 396.152	2.31 ± 0.09	90.0	100.18 ± 1.32	100.65 ± 1.55
6	Ni 216.556	0.15 ± 0.03	49.0	99.62 ± 0.85	98.93 ± 1.45
7	Zn 213.856	2.45 ± 0.16	6.5	98.28 ± 1.21	99.13 ± 1.80
8	Cu 324.754	0.20 ± 0.05	21.0	103.12 ± 2.11	102.87 ± 1.50
9	Sr 407.771	0.29 ± 0.06	0.8	100.30 ± 1.88	97.88 ± 1.20
10	Mn 257.610	0.19 ± 0.04	6.0	100.45 ± 0.98	101.27 ± 0.92
11	Ti 323.452	0.08 ± 0.02	18.0	102.10 ± 1.21	101.56 ± 0.99
12	Co 228.616	0.12 ± 0.08	22.0	101.50 ± 1.78	99.27 ± 1.50
13	Ba 455.403	0.08 ± 0.01	2.0	100.86 ± 1.75	98.05 ± 1.25

*Standard deviation of the results of five replicates.

safe in destroying complete organic matrix of opium by closed microwave digestion process. The closed vessel (TFM) microwave digestion was not performed with sulfuric acid and nitric acid was used because the boiling point of the nitric acid is less than the melting point of TFM. The wavelength of each element was identified using the Image Navigation Software of the ICP-OES instrument, which scans the entire spectrum from 180 nm to 495 nm in 2 min. In order to validate the proposed analytical method, a recovery study of 13 elements was taken up by spiking 5 μg/cm^3 and 10 μg/cm^3 of standards, respectively, into the opium samples and the samples were subjected to microwave dissolution; the results show identical recovery fractions for both the spiked samples. The analytical results of opium sample and the recovery fraction along with standard deviation of five replicates are given in Table 3. The results show that the method is having good reproducibility. The results of all elements except silicon show the recovery in the range of 97—103 %. In case of silicon the recovery was in the range of 85—86 %. The decrease in silicon recovery fraction may be attributed to the presence of HNO$_3$ and the absence of HF during the dissolution. The results of recovery study show that the technique is highly reliable and accurate. The concentration of each element in blank solution throughout analytical procedure was less than ICP-OES detection limits. The detection limits of the elements in the sample solution are given in Table 3.

REFERENCES

1. Bryant, R. J., *Chem. Ind. 5*, 146 (1998).
2. Remberg, B. and Nikiporov, A., *Bulletin of Narcotics XLVI*, 2, 79 (1994).
3. Wijesekera, R. I., Henry, K. D., and Rana Singhe, P., *Forensic Sci. Int. 36*, 193 (1998).
4. Maurice Pinto, U.N. Secretariat, ST/SOA/SER.K./63/ Rev. (1957).
5. Permuted, A. and Waller, T., U. N. Secretariat, ST/SOA/SER.K. 23 (1954).
6. Bartelet, J. C. and Farnilo, C., U. N. Secretariat, ST/SOA/SER.K. 30 (1954).
7. Evans, J. A. and Waller, W. N., *Forensic Sci. Soc. J. 4*, 189 (1966).
8. Thompson, J. W., *Analyst 86*, 829 (1961).
9. Schramal, P. and Xu, Li. Quiay, *Anal. Chem. 314*, 671 (1983).