

Energy

Robust and sensitive determination of multi-elements in *N*-methyl-2-pyrrolidone (NMP) using ICP-OES

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Goal

To demonstrate the suitability of the Thermo Scientific™ iCAP™ PRO Series ICP-OES, equipped with the Thermo Scientific™ iSC-65 Autosampler for sensitive, accurate, robust, and fully automated analysis of trace elements in *N*-methyl-2-pyrrolidone (NMP).

Introduction

N-methyl-2-pyrrolidone (NMP, density 1.028 g·cm⁻³) is a key solvent used in the manufacturing process of lithium-ion batteries for steps such as dissolving, binding, and cleaning.¹ It is an ideal solvent for these steps due to its high chemical and thermal stability, as well as miscibility in both aqueous as well as organic phase. NMP is also widely used in current processes established for battery recycling, but developments focus on potentially replacing this solvent with greener alternatives.² However, it is a potential concern from a health and safety perspective and must be handled such that it cannot endanger the environment or any person interacting with it in a process.

Inductively coupled plasma–optical emission spectroscopy (ICP-OES) is widely used as the analytical technique of choice for the analysis of trace elements in organic solvents, as it provides the robustness to cope with the organic matrix with only small modifications to the sample introduction system. ICP-OES allows the simultaneous determination of a wide range of trace elements with very good sensitivity, with typical detection limits in the µg·L⁻¹ concentration range.

There are challenges for the direct analysis of NMP analysis using ICP-OES without dilution. Due to the chemical properties of NMP, it may dissolve/damage the peristaltic pump tubing or autosampler probe parts, meaning analysis often must be performed manually. Therefore, often only self-aspiration of the sample is suitable, so that an inert, but rigid material like perfluoroalkoxy polymers (PFA) can be used. However, reliable and ideally automated operation of an analytical system is a key requirement in a production supporting laboratory.

In addition, the matrix can have a significant impact on the frequency of maintenance intervals due to the high amount of carbon content of such samples. For some elements, such as sulfur, phosphorus, lead, and cadmium, interferences and sensitivity requirements can be challenging due to spectral overlap and because the primary emission line falls in the less sensitive ultraviolet region.

This application note highlights an optimized analytical method for the analysis of NMP samples using the Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo instrument and the iSC-65 Autosampler for a fully automated analysis. A thorough validation of the method and the configuration were performed that included analysis of quality control standards, accuracy, and precision of measurements as well as analysis of cathode materials exposed to NMP.

Experimental

An iCAP PRO XP ICP-OES Duo instrument was used for the analysis of trace elements in NMP. Direct analysis was tested without any dilution, and alternatively, using a 10-fold dilution with ultra-pure water. The iCAP PRO XP ICP-OES was selected for this work as it provides full access to all parameters commonly used to optimize a method, and in addition, allows for short integration time and optimized performance for analytes emitting in the UV range of the spectrum thanks to the extended UV (or eUV) mode. An auxiliary gas flow using a mixture of 20% oxygen in argon was added to the plasma to facilitate plasma stability when analyzing NMP without dilution.

For the analysis of organic solvents, the choice of the right peristaltic pump tubing material is crucial. The peristaltic pump assures continuous aspiration of the sample and removal of the waste from the spray chamber. At the same time, the tubing material must not contaminate the sample by leaching out trace elements. In this study, three different types of peristaltic tubing were tested for chemical compatibility with NMP without and after 10-fold dilution with ultra-pure water. This test is highly relevant to enable an automated sample delivery for the analysis of longer analysis sequences. Three different peristaltic pump tubing materials (A: Tygon™, B: PVC, and C: Viton™) were tested for their resistance towards NMP.

For each of the tubing materials, a 1 cm long sample was soaked in both undiluted and 10-fold diluted NMP for 24 hours. The Tygon and PVC tubing dissolved completely in undiluted NMP, whereas the Viton tube expanded to almost twice of its original size. This confirms that the analysis of undiluted NMP is only feasible without the use of a peristaltic pump as no chemically compatible material could be found. On the other hand, all tubing materials exposed to 10-fold diluted NMP remained in shape. However, leaching of trace elements as contamination was observed when measuring the remaining NMP used for this test. The Viton tubing released significant levels of calcium, magnesium, sodium, and potassium, whereas $\mu\text{g}\cdot\text{L}^{-1}$ levels of zinc were released from the PVC pump tubing. As a conclusion of this experiment, the Tygon peristaltic pump tubing seemed to be the best way to facilitate automatable analysis of diluted NMP. Figure 1 and Table 1 summarize the observations of the experiments.

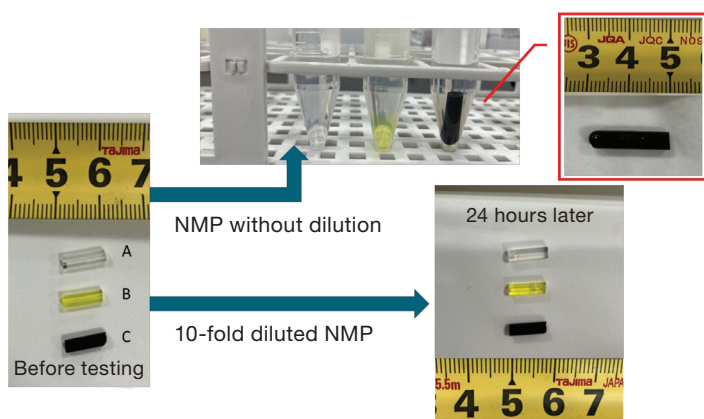


Figure 1. Testing procedure of the peristaltic pump tubing with NMP

Table 1. Summary of the peristaltic pump tubing resistance test

Sample name	Material (color)	Exposure to undiluted NMP for 24 hours	Exposure to 10-fold diluted NMP for 24 hours	Leaching in 10-fold diluted NMP
A	Tygon (clear)	Dissolved		Not observed
B	PVC (yellow)	Dissolved	No adverse effects observed	$5 \mu\text{g}\cdot\text{L}^{-1}$ Zn
C	Viton (black)	2 times expansion in size		$20 \mu\text{g}\cdot\text{L}^{-1}$ of K, $150 \mu\text{g}\cdot\text{L}^{-1}$ of Mg and $60 \mu\text{g}\cdot\text{L}^{-1}$ of Ca

Details of the sample introduction setup and applied instrument settings can be found in Table 2. For automation of the sample introduction using a 10-fold diluted NMP, the iSC-65 Autosampler was used.

Table 2. iCAP PRO XP ICP-OES instrument parameters (optimized for organic samples)

Parameter	Analysis of undiluted NMP	Analysis of 10-fold diluted NMP
Sample delivery	Manual, self-aspiration	Automated, using iSC-65 Autosampler
Peristaltic pump tubing	Sample: PTFE capillary Drain: Viton tube	Sample and Drain: Tygon tube
Peristaltic pump speed	30 rpm	45 rpm
Torch	Quartz	Quartz
Centre tube size and material	1.0 mm i.d., quartz	2.0 mm i.d., quartz
Spray chamber	Organic spray chamber	Glass cyclonic
Nebulizer	Concentric nebulizer self-aspirated	Concentric nebulizer
RF power	1,250 W	1,250 W
Coolant gas flow	13.5 L·min ⁻¹	13.5 L·min ⁻¹
Aux gas flow	0.55 L·min ⁻¹	0.50 L·min ⁻¹
Additional gas flow (O ₂ 100%)	0.05 L·min ⁻¹	–
Additional gas connected to	Auxiliary gas	–
Nebulizer gas flow	0.35 L·min ⁻¹	0.55 L·min ⁻¹
Exposure time for all modes	5 s	5 s
Uptake time	20 s	35 s
Wash out time	30 s	30 s
Total analysis time (including uptake and wash out)	1 min 15 s*	1 min 13 s*

*Simultaneous assessment of 89 different wavelengths

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to create LabBooks for sample analysis, data acquisition, processing, and reporting. The intuitive wavelength selection tool of the Qtegra ISDS Software, along with inspection of subarray plots and full frame images, was carried out to select interference-free wavelengths in standard solutions. In addition, the flexibility of Qtegra ISDS Software allows the creation of customized analysis methods, selecting both analysis range intelligent full range (IFR) and the eUV mode for the ultraviolet wavelength range in a single aspiration of a sample. The enhanced ultraviolet (eUV) analysis mode can further enhance the sensitivity for elements with emission lines in the ultraviolet wavelength range from 167.021 to 240.063 nm, such as sulfur, phosphorus, lead, and cadmium.

Sample preparation

Precleaned perfluoroalkoxy alkanes (PFA) bottles were used for the preparation. All blanks, calibration standards, and quality control samples (QC, CCV (continuing calibration verification)) were made from stock solutions prepared from single element standards (SPEX™ CertiPrep™, Metuchen, NJ, USA), in both NMP and 10-fold diluted NMP to result in the concentrations listed in Table 3. For the long-term analysis, 10-fold diluted NMP samples were used, as the use of a peristaltic pump is only possible this way, as previously investigated. For rinsing of the probe and sample delivery lines for both undiluted as well as diluted NMP, ultra-pure water was used.

Table 3. Concentrations of calibration solutions, QC, and sample spike recovery test. All numbers are in µg·L⁻¹.

Element	Standard calibration range	CCV	Spike recovery
Li, Co, Mn, Ni, Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mo, Na, Pb, Sn, Ti, V, Zn, K	25–100	25	25
S, P, Si	100–10,000	100	100

To improve accuracy and compensate for potentially occurring instrument drift during longer sequences, internal standardization was applied. Yttrium was spiked at a concentration of 1,000 µg·L⁻¹ to each blank, standard, or sample, and used as internal standard in the experiment.

Analysis of real samples

To simulate a typical sample, two pieces of a commercially available cathode material (homogeneously distributed on an aluminum-based substrate, Sigma-Aldrich) of each 1.0 cm x 1.5 cm size, as well as two additional pieces of only the substrate (but the same size) were soaked in undiluted NMP for 1 hour and 24 hours, respectively. One of the samples had visible damage in the surface of the surface, most likely caused during sample handling.

As mentioned before, NMP is a versatile and highly potent solvent, which may attack the material of vessels and containers used for sample handling. To account for any leaching even from a generally inert material such as PFA, a preparation blank was prepared under the same conditions as the cathode materials. All samples were diluted with ultra-pure water before being placed on the autosampler for analysis. Table 4 summarizes the details of the test.

Table 4. The sample detail of the cathode simulation test

Item	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Sample condition	PFA vessel	Aluminum substrate #1	Aluminum substrate #2	Cathode without damage	Cathode with damage
Duration	1 hour and 24 hours exposure time				

Result and discussion

Sensitivity (LOD) and linearity

Sensitivity and linearity for all analytes were determined from the analysis of the calibration blank and solvent standards. Table 5 shows the selected wavelengths and the obtained linearity with coefficient of determination $R^2 > 0.9991$ over the calibration range (Table 3) as well as the obtained limits of detection. The LODs were calculated as three times the standard deviation of ten replicate

measurements of the calibration blank. The MDLs of 10-fold diluted NMP are based on the determined LODs and reflect the dilution factor. Please note that the enhanced eUV mode can be used to further enhance sensitivity for elements that fall in the wavelength range of 167.021 to 240.063 nm. The intelligent Full Range (iFR) mode can measure the full wavelength range between 167.021 to 852.145 nm in one simultaneous measurement, which would allow reduction of the analysis times if required.

Table 5. Quantification results for both NMP and diluted NMP, as well as coefficient of determination (R^2), LODs, and MDLs. Note: Not all 89 wavelengths measured are reported in this table.

Analyte	Wavelength (nm)	Analysis mode	Yttrium internal standard wavelength (nm)	10-fold diluted NMP			Undiluted NMP	
				R^2	LOD ($\mu\text{g}\cdot\text{L}^{-1}$)	MDL ($\mu\text{g}\cdot\text{L}^{-1}$)	R^2	LOD ($\mu\text{g}\cdot\text{L}^{-1}$)
Ag	338.289	Aqueous-Axial-iFR	371.030	0.9999	1.61	16.1	0.9999	3.2
Al	167.079	Aqueous-Axial-eUV	224.306	0.9999	0.08	0.8	>0.9999	1.5
B	249.773	Aqueous-Axial-iFR	371.030	>0.9999	0.46	4.6	>0.9999	0.9
Ba	455.403	Aqueous-Axial-iFR	371.030	0.9999	0.09	0.9	0.9999	0.5
Ca	396.847	Aqueous-Axial-iFR	371.030	0.9999	0.09	0.9	>0.9999	0.1
Cd	226.502	Aqueous-Axial-eUV	224.306	>0.9999	0.08	0.8	>0.9999	0.6
Co	228.616	Aqueous-Axial-iFR	371.030	0.9998	0.47	4.7	0.9998	1.3
Cr	283.563	Aqueous-Axial-iFR	371.030	0.9999	0.50	5.0	>0.9999	0.7
Cu	324.754	Aqueous-Axial-iFR	371.030	0.9999	0.99	9.9	>0.9999	0.8
Fe	238.204	Aqueous-Axial-eUV	224.306	0.9995	0.17	1.7	>0.9999	0.7
K	766.490	Aqueous-Axial-iFR	371.030	>0.9999	0.58	5.8	0.9995	14.6
Li	670.776	Aqueous-Axial-iFR	371.030	0.9998	0.29	0.3	0.9999	0.6
Mg	279.553	Aqueous-Axial-iFR	371.030	0.9998	0.02	0.2	>0.9999	0.1
Mn	257.610	Aqueous-Axial-iFR	371.030	0.9999	0.09	0.9	>0.9999	0.1
Mo	202.030	Aqueous-Axial-eUV	224.306	>0.9999	0.75	7.5	0.9999	6.8
Na	589.592	Aqueous-Axial-iFR	371.030	0.9999	0.19	1.9	0.9904	22.0
Ni	221.647	Aqueous-Axial-eUV	224.306	0.9999	0.52	5.2	0.9998	5.2
P	177.495	Aqueous-Axial-eUV	224.306	0.9999	5.48	54.8	0.9890	68.9
Pb	220.353	Aqueous-Axial-eUV	224.306	0.9998	1.54	15.4	0.9994	23.4
S	180.731	Aqueous-Axial-eUV	224.306	0.9999	9.50	95.0	0.9993	295.9
Si	251.611	Aqueous-Axial-iFR	371.030	0.9999	1.51	15.1	0.9996	5.1
Sn	189.989	Aqueous-Axial-eUV	224.306	0.9995	2.85	28.5	0.9842	45.0
Ti	334.941	Aqueous-Axial-iFR	371.030	0.9999	0.26	2.6	0.9991	0.6
V	292.402	Aqueous-Axial-iFR	371.030	0.9999	0.38	3.8	>0.9999	1.0
Zn	202.548	Aqueous-Axial-eUV	224.306	>0.9999	0.10	1.0	>0.9999	0.7

A comparison of the results between the analysis of undiluted versus diluted NMP shows that for most elements, the dilution required to allow for the use of automated sample delivery translates directly into the attainable MDLs. For some elements however, in particular lead, phosphorous, sulfur, tin, and potassium, the MDLs obtained in 10-fold diluted NMP exceed those obtained in the undiluted solvent. This is due to the reduced observation of interference from the carbon-based sample matrix and the thus resulting lower background.

Accuracy, precision, and robustness

For reliable analysis in a testing laboratory, it is important that the results obtained are accurate and precise also in longer batches comprising different sample types. Commonly, spike recovery for selected samples or QC standards containing a known

concentration of all analytes are analyzed periodically during a sample batch to monitor method performance. To evaluate the accuracy and precision for this method, spike recovery tests were performed using diluted NMP, spiked at the concentration level of the first calibration standard for all analytes. The results demonstrate excellent accuracy with recovery values between 95% and 110%. RSD (%) of 10 replicates of the spiked sample were found to be below 3%. The results are summarized in Table 6.

Whereas for most elements, no leaching or extraction was observed in NMP regardless of the exposure time, the sample with a damaged surface showed a significant increase in the observed levels of lithium, manganese, and nickel, but also sulfur, and, to a lesser extent, phosphorous.

Table 6. Spike recovery results for a 10-fold diluted NMP samples

	Spike recovery test (%)			
	Exposure time 1 hour		Exposure time 24 hours	
	Sample 4 + spike (n=10)	Sample 5 + spike (n=10)	Sample 4 + spike (n=10)	Sample 5 + spike (n=10)
Ag	96	96	95	97
Al	106	108	109	110
B	98	98	100	99
Ba	103	102	104	104
Ca	103	102	104	104
Cd	101	101	102	102
Co	103	101	106	103
Cr	102	101	102	103
Cu	96	94	96	96
Fe	93	92	93	94
K	95	96	96	96
Li	106	106	110	113
Mg	104	103	104	105
Mn	104	102	108	105
Mo	99	98	99	99
Na	98	100	99	100
Ni	107	105	104	109
P	105	105	101	103
S	102	109	105	101
Si	96	97	94	97
Sn	95	102	91	95
Sn	97	95	97	99
Ti	103	104	102	104
V	104	104	104	105
Zn	100	100	101	101

To evaluate robustness, a batch containing a total of 236 samples was scheduled for analysis. Following 10 unknown samples, a quality control standard (continuing calibration verification, CCV, concentration details are shown in Table 3) was analyzed and the results as well as the response of the internal standard were monitored. In summary, 21 CCVs were analyzed in approximately 4.5 hours using both iFR and eUV modes. Figure 2 shows the results obtained for the CCV samples. The relative standard deviation of all CCVs analyzed (n=21) in the batch was found to

be generally below 1.5% (with the exception of aluminum, which was found to be less than 3% RSD) for both modes Axial iFR and Axial eUV and indicates that the iCAP PRO XP Duo ICP-OES allows for robust and reliable long-term analysis of this matrix.

The response of the internal standards is shown in Figure 3. The internal standard showed excellent recovery (within approximately 94% to 103%) over the entire runtime of the batch, demonstrating robust analytical performance.

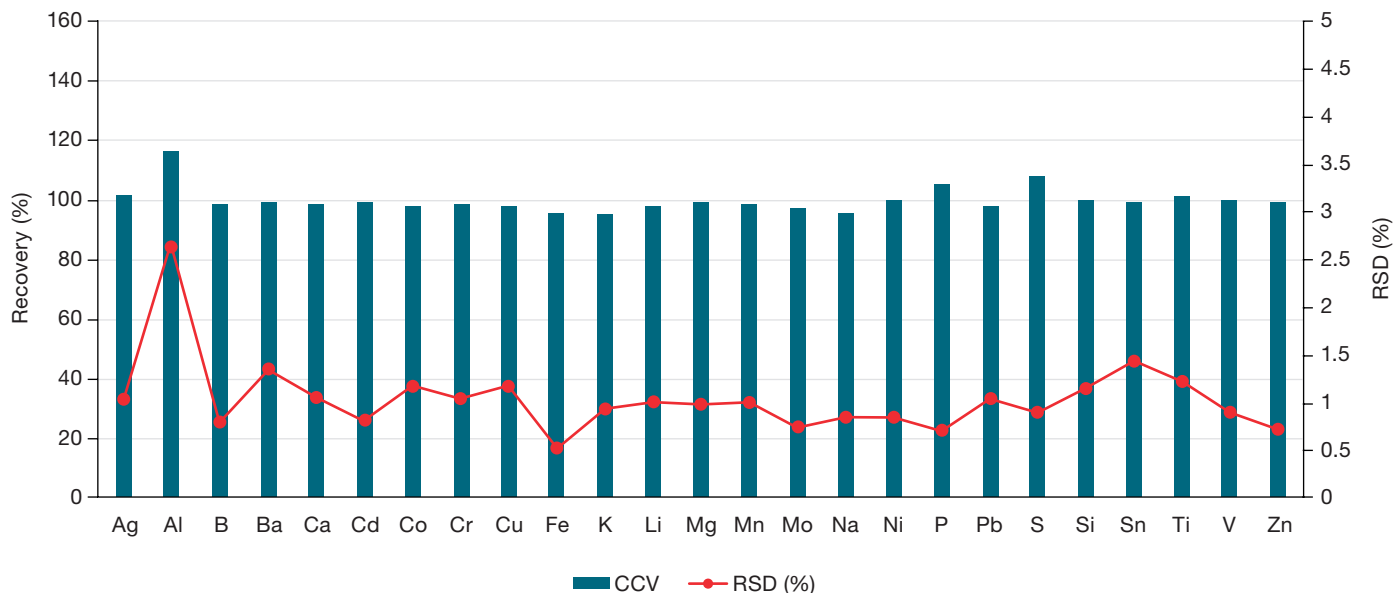


Figure 2. QC calibration verification results (n=21). CCVs recovery and orange line is RSD (%) of n=21.

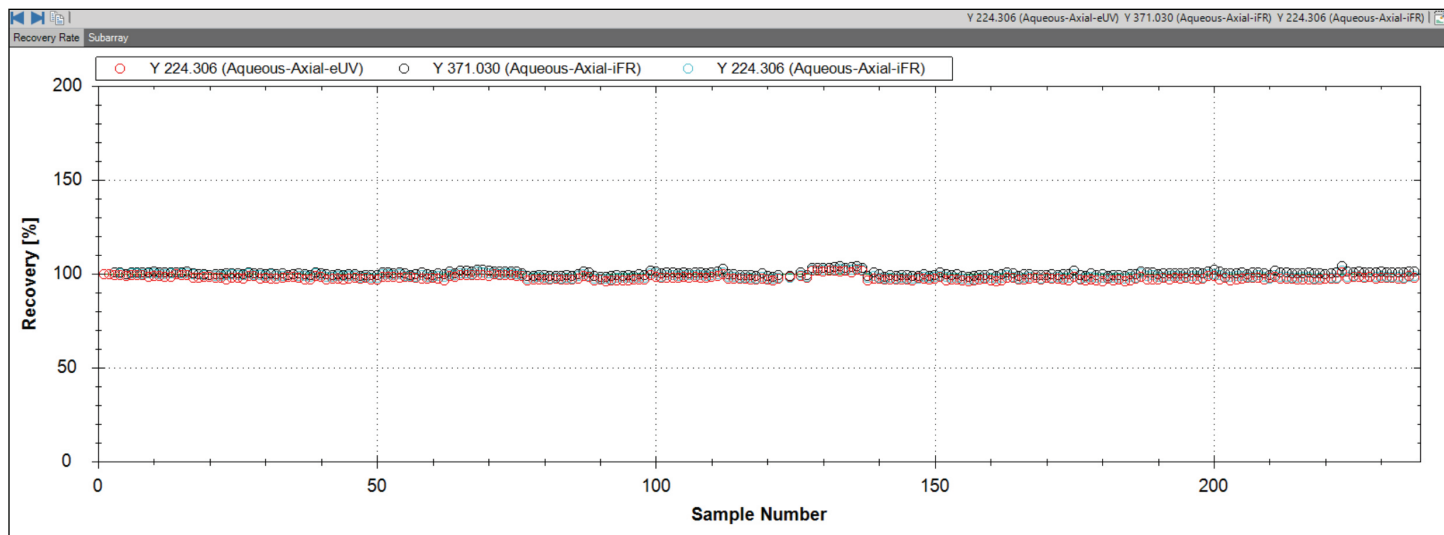


Figure 3. Response of the internal standard (yttrium) assessed over a period of ~4.5 hours of uninterrupted acquisition for 236 of a 10-fold diluted NMP samples matrix analysis

Conclusion

The iCAP PRO XP ICP-OES Duo instrument together with the iSC-65 Autosampler were employed to analyze 25 elements in NMP following simple dilution with ultra-pure water. The dilution was required to avoid adverse effects of this powerful solvent towards the peristaltic pump tubing, and therefore ultimately to allow for an automated workflow. The results showed that the analysis can be easily performed and automated using the proposed methodology to yield high accuracy and excellent analytical robustness.

This analytical method was rigorously tested, and the results obtained clearly demonstrate the following analytical advantages as a fully automated analysis:

- High sensitivity was achieved even for challenging but critical analytes such as sulfur, phosphorous, cadmium, or lead, commonly emitting in the UV range of the spectrum. Excellent spike recovery results (generally less than $\pm 1.5\%$) and QC CCV results (RSD within 3%) were obtained, demonstrating the accuracy and precision of the analysis.
- Automation of the workflow was feasible using the iSC-65 Autosampler following a minimum dilution of NMP with ultra-pure water.
- Robust and stable analytical performance was demonstrated over 4.5 hours of continuous acquisition of 236 NMP samples, with no maintenance required.

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