Application note | 000773

Industrial analysis

Stay ahead in developing green energy solutions: Fatty acid methyl ester (FAME) analysis for jet fuel using gas chromatography-mass spectrometry

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Keywords

Biofuels, fatty acid methyl esters (FAMEs), green energy, robust response, high throughput, IPA 585 method, GC-MS

Goal

The goal of this application note is to highlight the suitability of the Thermo Scientific™ ISQ™ 7610 single quadrupole GC-MS system to deliver robust and accurate quantification of FAMEs in fuel samples according to Method IP 585.

Introduction

As the world's energy demands continue to increase, new sources of energy are needed to replace dwindling fossil fuel resources. Biofuels, such as biodiesel, offer an attractive alternative to solve the ever-growing energy crisis. Consisting of fatty acid methyl esters (FAMEs) chemically derived from vegetable oils and animal fats, biodiesel provides a renewable energy resource. As carbon sources to produce biodiesel originate from the surrounding environment, combustion of biodiesel helps close the carbon cycle and move towards a carbon neutral society.[1] In addition, life cycle analysis shows a significant reduction in harmful environmental impacts (i.e., emissions, waste products) in production of new-generation biodiesels compared to fossil fuels;[2] further increasing their attractiveness as a replacement energy resource.

The transportation sector consumes up to 60% of the world's oil reserves,[3] making it ideal for the implementation of biofuels. Despite similarities between biofuels and their fossil fuel counterparts, small differences in physical/chemical properties have posed challenges for the implementation of biofuel, particularly in the aviation sector. FAMEs possess a lower freezing point in comparison to fossil fuels and can solidify in fuel lines and filters (also known as fuel gelling) at low temperatures present at high altitudes, thus causing unsafe flying conditions. Resistance and tolerance of engine components is also problematic, particularly in older engines. FAMEs can oxidize or corrode metal components and dissolve elastomer-based materials, such as tubing or sealings, causing potential engine rupture over long exposures.[1]

Research has shown that blending biodiesel with traditional petroleum-based jet fuels can help mitigate these risks in engine operation. However, to ensure absolute safety in daily aviation operations, the current allowable limit for FAMEs content within jet fuel is 50 mg·kg^{-1} (increased from 5 mg·kg^{-1} in 2015). Contamination of jet fuel by FAMEs can occur during transport through pipeline infrastructure shared with biodiesel used in other sectors. As the FAME composition depends on the application and type of plant/animal sources used, the content present in jet fuels can vary, requiring accurate quantification over large concentration ranges. The petroleum hydrocarbon matrix also poses analysis challenges, where efficient separation and selective detection between FAMEs and relatively non-polar sample matrix is needed to avoid interferences.

This application note will follow Method IP 585, established by the Energy Institute, for the analysis of FAMEs in jet fuels. As part of the method validation, linearity was assessed using two calibration ranges, which resulted in accurate and reliable results. The ISQ 7610 single quadrupole GC-MS system, equipped with the new XLXR™ detector, was able to deliver accurate quantification over large concentration ranges without the need of multiple calibration curves. The system provided robustness in large sample sequence analyses, without drift in peak shape or retention time, with sustained ion source sensitivity over multiple sample batches without requiring source maintenance in between.

Experimental

Standard and sample preparation

Calibration standards were prepared as described in Method IPA 585.[4] Briefly, a 1,000 mg·kg^{-1} stock solution containing palmitic acid methyl ester (C16:0), heptadecoaoic acid methyl ester (C17:0), stearic acid ethyl ester (C18:0), methyl *cis*-9-octadecenoate (C18:1), linoleic acid methyl ester (C18:2), and linolenic acid methyl ester (C18:3) (AccuStandard, USA) was diluted in a 1:10 ratio in dodecane to produce a secondary stock solution of 100 mg·kg^{-1}. Serial dilution of the secondary stock solution was performed to produce calibration standards (2, 4, 6, 8, 10, 20, 40, 60, 80, and 100 mg·kg^{-1}). To each calibration standard, methyl heptadecanoate-d_{33} (1,000 mg·kg^{-1}, AccuStandard) was added as an internal standard to produce a final concentration of 10 mg·kg^{-1} in each calibration standard.

To evaluate method performance, kerosene (Fisher Scientific, USA) was used as a surrogate matrix to mimic jet fuel and spiked with the FAME stock solution at 5 and 50 mg·kg^{-1} concentration levels.

Instrument and method setup

Standards and kerosene spiked samples were analyzed using the ISQ 7610 GC-MS. Automatic sample injection was performed using a Thermo Scientific™ TriPlus™ RSH autosampler, with chromatographic separation obtained using a Thermo Scientific™ TRACE™ 1610 GC equipped with a Thermo Scientific™ TRACE™ TR-FAME 60 m x 0.25 mm i.d. x 0.25 µm film capillary column (P/N 260M154P). Sample analysis was performed using simultaneous full scan and targeted-selected ion monitoring (t-SIM) acquisition. Additional details of instrument parameters are displayed in Tables 1 and 2.

Table 1. GC injection and column conditions

TRACE 1610 GC system parameters	
Injection volume (µL)	1
Liner	Thermo Scientific™ LinerGold™ Split/Splitless with Quartz Wool (P/N 453A2265-UI)
Injector type	Thermo Scientific™ iConnect™ SSL
Injection mode	Split
Split ratio	1:10
Injector temperature (°C)	260
Carrier gas, (mL·min^{-1})	He, 0.8 (constant flow)
Oven temperature program	
Initial temperature (°C)	150
Hold time (min)	5
Temperature 1 (°C)	210
Rate (°C·min^{-1})	3
Hold time (min)	0
Temperature 2 (°C)	252
Rate (°C·min^{-1})	15
Hold time (min)	3
Total run time (min)	31

Table 2. Mass spectrometer conditions for using simultaneous full scan/timed acquisition (t-SIM)

ISQ 7610 single quadrupole GC-MS parameters	
Transfer line temperature (°C)	260
Thermo Scientific™ ExtractaBrite™ ion source temperature (°C)	300
Ionization mode	EI
Electron energy (eV)	70
Full scan range (*m/z*)	50–550
Full scan time (s)	0.08
SIM time (s)	0.3
Minimum baseline peak width (s)	3
Desired peak scans	10

Results and discussion

Chromatography and sensitivity

Using the TRACE TR-FAME capillary column and oven temperature program described here, separation from the hydrocarbon matrix within kerosene was achieved showing minimal impact on full scan analysis. All targeted compounds were efficiently separated in under 24 minutes using simultaneous full scan and t-SIM acquisition—a 20-minute reduction in analysis time compared to Method IP 585 (Figure 1A). Quantification of FAMEs below 1 mg·kg^{-1} was easily achieved using acquired t-SIM data (Figure 1B), providing trace-level sensitivity well below regulatory requirements (i.e., 50 mg·kg^{-1}).

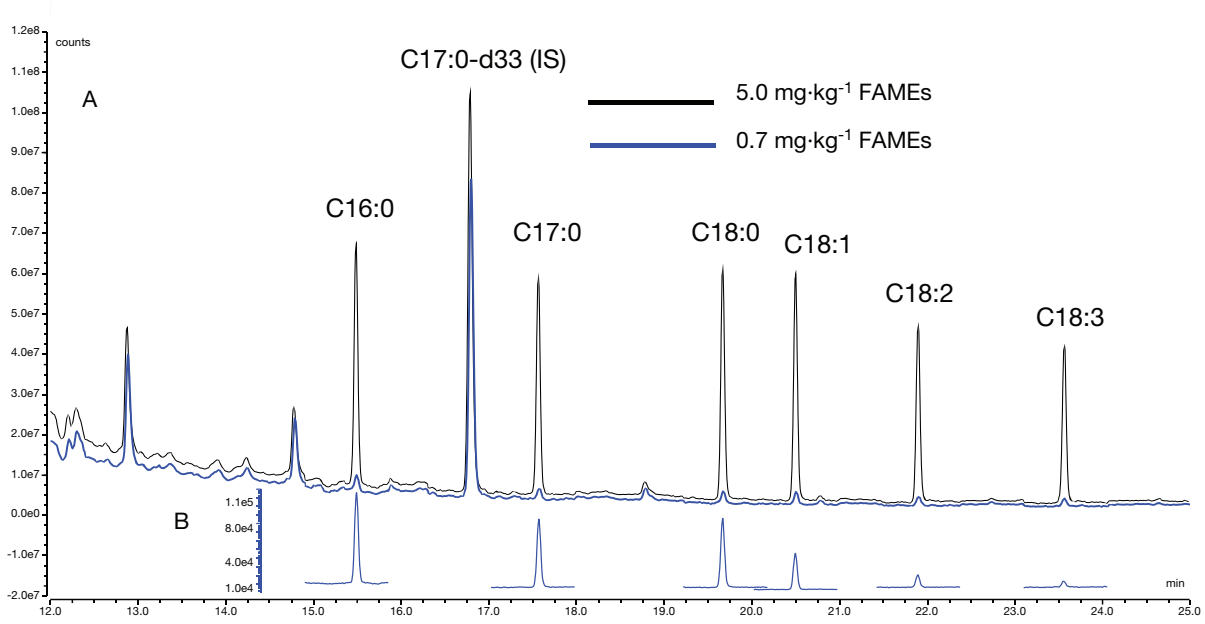

Figure 1. (A) Full scan acquisition of 0.7 and 5 mg·kg^{-1} FAMEs in kerosene and (B) t-SIM acquisition of FAMEs of 0.7 mg·kg^{-1} FAMEs in kerosene

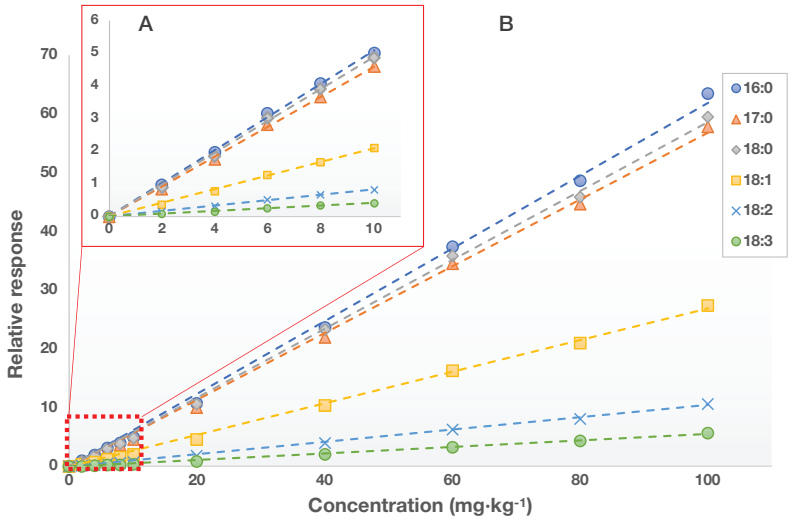

Figure 2. Calibration curves obtained for FAMEs in the (A) low calibration range (2–10 mg·kg^{-1}) and (B) entire calibration range (2–100 mg·kg^{-1})

Table 3. Retention time, acquisition ions, and correlation coefficients for the low, high, and entire calibration range for FAMEs

Compound	Retention time (min)	SIM ions[a]	Low calibration (2–10 mg·kg^{-1})		High calibration (20–100 mg·kg^{-1})		Overall calibration (2–100 mg·kg^{-1})	
			r^2	slope	r^2	slope	r^2	slope
C16:0	15.52	**227,** 270, 239	0.9995	0.51	0.9992	0.62	0.9989	0.62
C17:0-d33 (IS)	16.82	**286,** 317, 267	N/A	N/A	N/A	N/A	N/A	N/A
C17:0	17.61	**241,** 284, 253	0.9995	0.46	0.9994	0.57	0.9991	0.57
C18:0	19.73	**255,** 298, 267	0.9997	0.49	0.9995	0.59	0.9993	0.59
C18:1	20.57	**264,** 265, 296	0.9991	0.21	0.9993	0.27	0.9987	0.27
C18:2	21.97	**262,** 263, 294	0.9995	0.08	0.9992	0.10	0.9988	0.10
C18:3	23.60	**236,** 263, 292	0.9990	0.04	0.9986	0.06	0.9979	0.06

[a]Bold SIM ion represents quantification ion
IS – internal standard
r^2 – linear regression correlation coefficient
N/A- not applicable

Linearity

Results from the calibration analysis carried out using the criteria defined in Method IP 585 (forced origin) are shown in Figure 2 and Table 3. Implementation of two calibration ranges (low and high) within the method is attributed to differences in response factors between these concentration ranges, with higher response (i.e., slope) occurring at the higher concentration range (Table 3). However, excellent linearity was observed over the low (2–10 mg·kg^{-1}), high (20–100 mg·kg^{-1}), and entire calibration range (2–100 mg·kg^{-1}) for all FAME components investigated, with correlation coefficients surpassing the Method IP 585 criteria ($r^2 > 0.985$).

Method accuracy

Method accuracy and precision was evaluated through the analysis of the spiked matrix. The most commonly used jet fuels (i.e., Jet-A and Jet-1A) are kerosene based. Therefore, spiked concentrations at previous (5 mg·kg^{-1}) and current (50 mg·kg^{-1}) regulatory limits for FAMEs were prepared in kerosene as a surrogate matrix. Results from spike recoveries are shown in Figure 3.

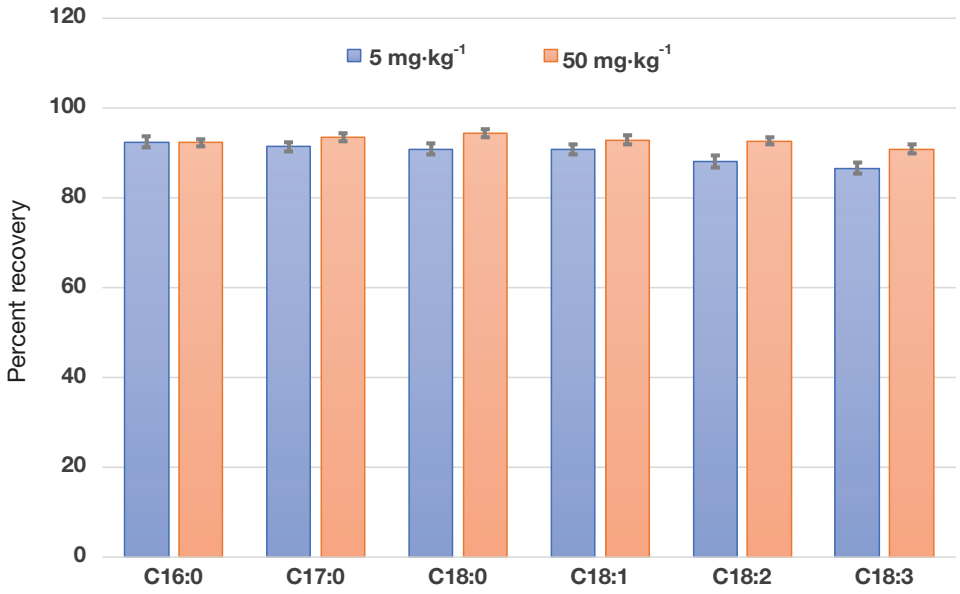

Figure 3. Spike recovery of 5 and 50 mg·kg^{-1} FAMEs in kerosene (n = 8)

Using the Method IP 585 criteria, spiked recoveries of 5 and 50 mg·kg^{-1} in kerosene samples were determined using the low and high calibration curves, respectively. Spike recoveries were 87–92% and 91–94% for 5 and 50 mg·kg^{-1}, respectively, with standard deviation between replicates (n = 8) ≤ 1.3% at both spike levels.

For everyday analysis of FAMEs in jet fuels, use of a single calibration curve over the entire investigated range is ideal. This aids in the implementation of automated quality assurance/control procedures, reduces sample processing time, and increases productivity. Using the criteria outlined in Method IP 585, the concentration of FAMEs was underestimated in kerosene samples spiked at 5 mg·kg^{-1} when using the entire calibration range (2–100 mg·kg^{-1}), with calculated concentrations 64–76% of the original spiked amount (Table 4).

However, when implementing an offset calibration (i.e., not forced through 0) instead of a forced origin calibration as described in Method IP 585:

- Calculated concentrations of 5 mg·kg^{-1} FAMEs spiked in kerosene increased to 98–105% of the original spiked value.
- Comparable recoveries were observed at the high end of the calibration curve for 50 mg·kg^{-1} FAMEs spike in kerosene using both the Method IP 585 and offset calibration methods.
- Linear correlation coefficients improved with offset calibration for the entire calibration range (2–100 mg·kg^{-1}), demonstrating the high linear dynamic response of the new XLXR detector.

Robust and stable performance

Method efficiency and robustness over long analysis sequences are key for any analytical laboratory to minimize instrument downtime and maintain productivity. Extended analysis periods with injected matrix can cause chromatographic and detection performance to degrade, risking poor analysis quality at low concentrations. However, stable response was observed with more than 90 injections of kerosene spiked with 5 mg·kg^{-1} FAMEs with percent relative standard deviation (%RSD) ranging between 1.5 and 3.0%. In addition, no degradation of separation efficiency was observed after 96 injections of matrix with retention times and absolute response (i.e., peak area) remaining stable at regulatory limits for FAMEs in jet fuel (i.e., 50 mg·kg^{-1}, Figure 4).

Little change in the absolute response of FAMEs demonstrates the high in-sequence stability. However, maintaining performance stability while running multiple sequences over several days is of equal importance for laboratories involved in the quality control of fuels. Results shown in Figure 4 are from one of several sequences set up on the ISQ 7610 GC-MS system over a period of several days. To assess performance stability, a 60 mg·kg^{-1} calibration standard was injected after every 10th sample injection to evaluate ion source sensitivity and robustness over a 7-day period of continuous analysis (Figure 5).

After 230 injections of spiked kerosene matrix, the absolute sensitivity decreased by less than 10% from the initial intensity observed for the 60 mg·kg^{-1} standard. This once again highlights the robustness of the ExtractaBrite ion source over long analysis periods, allowing for increased uptime without source maintenance.

Table 4. Spike recovery and correlation coefficient comparison between forced and off-set origin with single calibration range

5 ppm spike recovery (%)		50 ppm spike recovery (%)		Correlation coefficient	
Forced (IP 585)	Offset	Forced (IP 585)	Offset	Forced (IP 585)	Offset
76	104	92	93	0.9989	0.9990
74	101	94	95	0.9991	0.9993
76	98	94	95	0.9993	0.9993
70	103	93	94	0.9987	0.9991
69	99	93	94	0.9988	0.9989
64	105	91	93	0.9979	0.9984

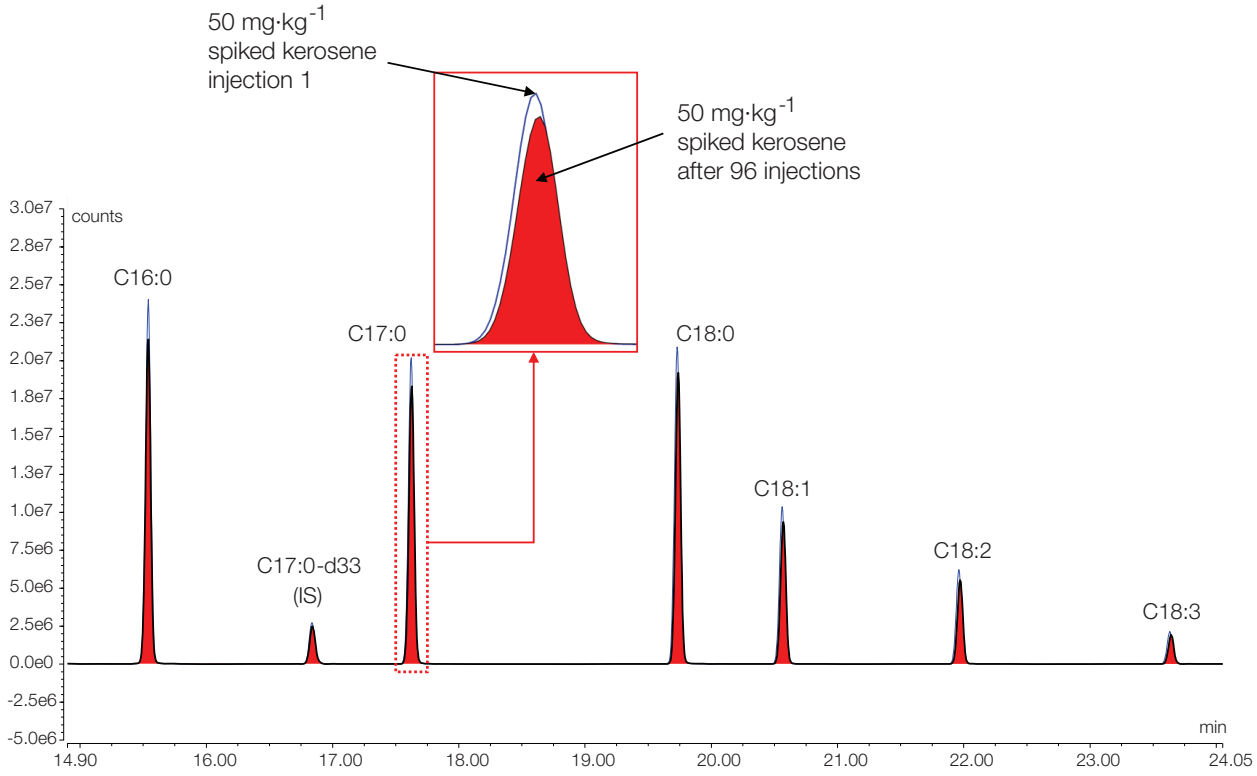

Figure 4. Comparison of total ion chromatograms of 50 mg·kg^{-1} FAME spike in kerosene after 1 and 96 injections

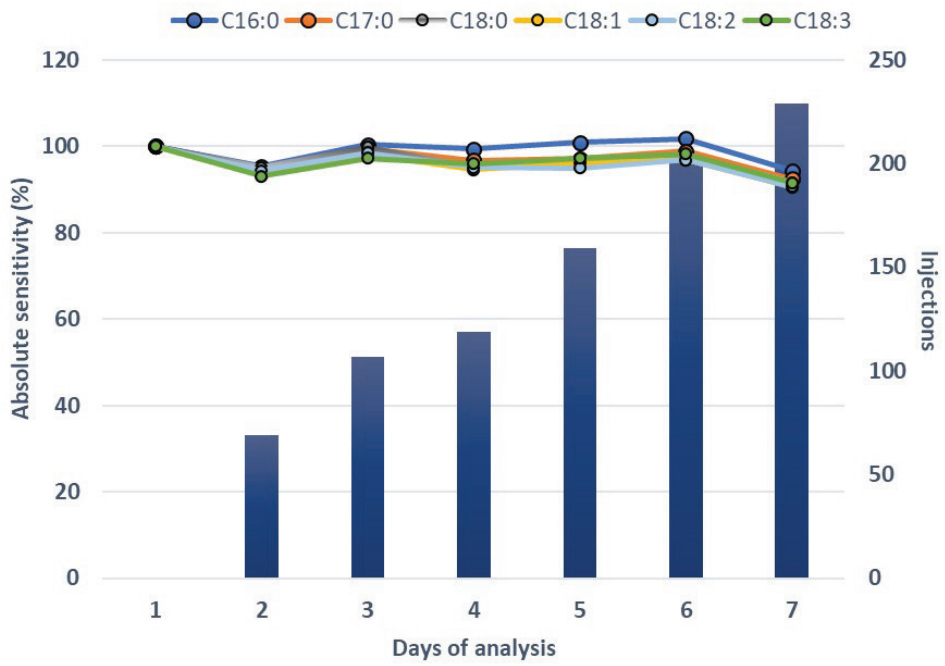

Figure 5. Absolute sensitivity robustness with continuous analysis over 7 days. Number of injections (bar graphs) represent the total number of injections from start of the analysis (day1).

Conclusion

This application demonstrates the ISQ 7610 MS, equipped with the new XLXR detector and coupled to the TRACE 1610 GC, provides a highly robust, efficient, and sensitive methodology required by laboratories for the routine analysis of FAMEs in jet fuels.

- Shorter analysis time was achieved using the TRACE TR-FAME capillary column, providing efficient separation of targeted FAMEs with a 20-minute reduction in analysis time compared to Method IP 585.
- Linear response was observed over low and high calibration ranges as well as over the entire calibration range, surpassing criteria defined by Method IP 585.
- Recoveries of 5 and 50 $mg \cdot kg^{-1}$ from spiked kerosene ranged from 87 to 94% with accurate quantification made possible using a single calibration curve with the high linear dynamic response of the new XLXR detector.
- Stable response of the ExtractaBrite ion source over a week with multiple injection sequences provides laboratories with increased uptime and productivity while delivering accurate detection of FAMEs at low $mg \cdot kg^{-1}$ levels.

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