

Chemical Stability Assessments of R-514A and R-1233zd(E)

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ABSTRACT

As the phase-out date for R-123 in developed countries approaches, alternative low pressure refrigerants are being identified and qualified for use in new and existing chiller products. This paper summarizes chemical stability evaluations that were conducted in the laboratory and in operating equipment to evaluate the system chemistry of refrigerant alternatives R-514A and R-1233zd(E).

R-514A is an azeotropic olefin blend comprised of 74.7% cis-1,1,1,4,4,4-hexafluorobut-2-ene (R-1336mzz(Z)) and 25.3% trans-1,2-dichloroethene (R-1130(E)). R-1233zd(E) is the single component olefin refrigerant trans-1-chloro-3,3,3-trifluoropropene. Chemical stability evaluations of the refrigerant, lubricant, and catalysts were conducted in sealed glass tubes according to ASHRAE Standard 97 to confirm acceptable chemical stability of the refrigerants relative to R-123. Chemical and physical stability of R-514A was monitored during the performance and endurance testing of two centrifugal compressor-based chillers. Results of the laboratory and system chemical stability evaluations, and potential system chemistry impacts on reliability and performance, are presented in this paper.

Chemical stabilities of refrigerants R-514A and R-1233zd(E) were proven to be better than R-123, and both refrigerants have been qualified for application in a range of centrifugal compressor-based chiller products. R-1233zd(E) has higher operating pressures than R-123 and is applied in new equipment designs. R-514A is a design-compatible replacement for R-123 in both engineered retrofit applications and in new production.

INTRODUCTION

R-123 (2,2-dichloro-1,1,1-trifluoroethane) is a low-pressure refrigerant primarily applied in centrifugal water-cooled chillers used for industrial air conditioning and climate control of large buildings and complexes. Along with other hydrochlorofluorocarbon (HCFC) refrigerants, R-123 is being phased out of use via control measures specified in the Montreal Protocol. For example, in the United States, R-123 is intended to be phased out of use in new equipment as of January 1, 2020. Recycled R-123 is expected to be available for service for the foreseeable future (EPA 2014). In alignment with the R-123 phaseout dates, alternative low pressure refrigerant candidates have been proposed, evaluated, and in some cases qualified, for use in existing and new equipment designs. Two of these alternates - R-514A and R-1233zd(E) – are the focus of this paper. Table 1 provides a summary of chemical structure, molecular weight, boiling point, and global warming potential (GWP) of both of the new refrigerants, along with the R-123 baseline for comparison purposes.

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Table 1. Refrigerant Properties

Refrigerant	Chemical Structure	Molecular Weight	Normal Boiling Point	GWP ¹
R-123		152.9 g/mol	28°C (82°F)	79
R-1233zd(E)		130.5 g/mol	18°C (65°F)	1
R-514A 74.7% R-1336mzz(Z) 25.3% R-1130(E)		139.6 g/mol	29°C (84°F)	2

¹GWP values are from the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC 2013).

Many factors must be considered in the evaluation of new refrigerants, including but not limited to, thermophysical properties, safety and environmental factors, business considerations such as availability and cost, and reliability factors including lubricant and material compatibility, and chemical stability. Chemical stability will be the primary focus of this paper, while separate papers address other factors of interest for R-1233zd(E) (Kujak et al. 2015) and R-514A (Schultz and Gallant 2016).

When selecting or designing a new refrigerant for HVACR applications, chemical stability must be understood. A refrigerant must maintain its chemical integrity in the presence of conditions and materials that it will be exposed to in operating equipment, such as the lubricant, the materials of construction, and potential contaminants. When assessing chemical stability of a new refrigerant, effort is initially focused on understanding potential refrigerant decomposition pathways and breakdown products, and the conditions under which decomposition may occur. These considerations are then applied to a risk assessment for the intended application(s) of the refrigerant. For highly pure, single-component refrigerants, this process is relatively straightforward. However, as additional factors that influence chemical stability are introduced - such as refrigerant manufacturing impurities, refrigerant blend components, lubricants, contaminants, and a range of system materials - the chemical stability assessments become more complex.

To better understand how different factors impact chemical stability of a specific refrigerant in operating equipment, controlled bench testing and in some cases system testing may be conducted. These tests are typically carried out sequentially to 1) validate the chemical stability risks in the presence of specific materials of interest, and 2)

verify the overall suitability of the refrigerant with all of the system materials in the target application.

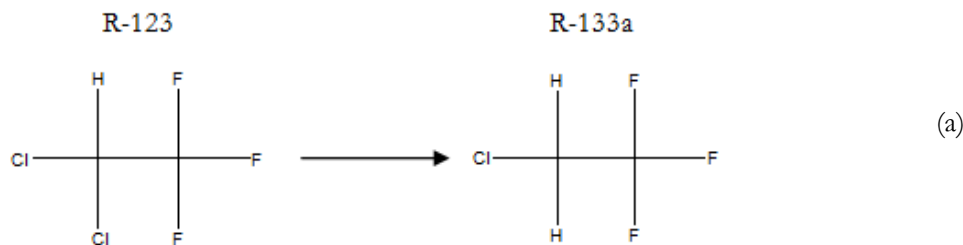
In the current landscape of limited refrigerant options that meet all of the imposed requirements, it is critical to apply a thorough, risk-based, application-focused approach to the consideration of refrigerant alternatives. This ensures that potentially viable candidates are not dismissed prematurely due to overly restrictive or irrelevant criteria, and that those candidates that demonstrate application potential undergo rigorous evaluation prior to implementation. In the future, this is likely to become even more important as the industry continues to explore new refrigerant chemistries.

Chemical stability of R-123 has been well-studied in the HVACR industry, as well as internally, and R-123 has been applied successfully in HVAC systems for decades. One of the most significant early studies conducted for the industry was that of Dietrich Huttenlocher in Materials Compatibility & Lubricant Research (MCLR) project #650-50200 which was summarized in the early 1990s (Huttenlocher 1992). In this study, Huttenlocher assessed the chemical and thermal stability of 22 HFC and HCFC refrigerant/lubricant mixtures. Six different HFC refrigerants and four different HCFC refrigerants - including R-123 - were combined with lubricants of interest and were aged in the presence of metal catalysts in sealed glass tubes at three different temperatures. Results confirmed that the six HFC refrigerants (R-32, R-125, R-134, R-134a, R-143a, and R-152a), and one of the HCFC refrigerants (R-22), were very stable and did not undergo thermal or chemical decompositions after exposure for two weeks at 200°C, while HCFC refrigerants R-124 and R-142b were less stable but still superior to the incumbent R-12. R-123 was found to be the least stable refrigerant investigated in Huttenlocher's study; however, it was determined to be at least 10 times more stable than R-11, the refrigerant it was intended to replace in low-pressure chiller applications. Thus, despite the lower chemical stability of R-123 relative to the other refrigerants assessed in the study, the transition from R-11 to R-123 was determined to be low risk from a chemical stability perspective. Internal bench and system testing of R-11 and R-123 conducted by Doerr, Kujak, and Steinke, corroborated these findings (Doerr et al. 1996).

The approach and logic applied historically to assess the chemical stability risks in the transition from R-11 to R-123, is similar to that applied herein to assess the risks of R-514A and R-1233zd(E) relative to R-123.

CHEMICAL STABILITY EVALUATIONS

Using the R-123 chemical stability results from Huttenlocher's study, and incorporating internal results from the same timeframe, Arrhenius plots were constructed to determine the conditions under which R-123 would be predicted to degrade at low but measurable levels. The goal was to evaluate the relative chemical stability of the new refrigerants under conditions known to induce degradation of R-123. In the presence of lubricant and metal catalysts, R-123 degrades according to the following reaction (a), with the higher pressure degradation product R-133a being the primary product.



Results from the Arrhenius plots based on R-133a formation indicated that temperatures within 5°C (9°F) of 135°C (275°F), 145°C (293°F), and 155°C (311°F) over a 1-week timeframe, correlated to predicted R-123 degradation of 0.5%, 1.5%, and 3.0%, respectively.

Chemical stability evaluations of R-123, R-1233zd(E), and R-514A with metal catalysts and lubricant were performed by exposing samples at these three different temperatures for one week and conducting post-exposure sample assessments. The goal of this study was to compare the degradation of R-123 under controlled conditions, to

the degradation of R-1233zd(E) and R-514A under these same conditions. After subjecting the fluids in the tubes to the accelerated thermal aging conditions, detailed analyses were performed on the exposed fluids. It is noteworthy that the initial chemistry review established that the olefin refrigerants do not follow the same degradation mechanisms as R-123 and R-11, which form the higher pressure degradation products R-133a and R-21, respectively. Thus, prior to carrying out this study, significant time and effort was spent ensuring that analytical procedures were in place to detect and measure lower pressure degradants resulting from olefin refrigerant decomposition.

Accelerated Reaction Study

Chemical stability evaluations were conducted using R-123 and R-1233zd(E) with white mineral oil, and R-514A with a polyol ester (POE) based lubricant. Each tube was prepared at 50% refrigerant/50% lubricant (by weight) and included three metal catalysts representing the system materials of construction – cast aluminum, carbon steel, and copper. Tubes were prepared according to the general procedure in ASHRAE Standard 97 (ASHRAE 2007), with a modification to the tube size specified in the standard. Larger tubes were utilized in this study to facilitate sufficient fluid volumes necessary for post-exposure testing.

Exposures were carried out at the three different temperatures for seven days (168 hours).

Post-exposure chemical stability assessments included tests of both the refrigerant and lubricant portions of the matrix. Prior to opening the tubes, the aged samples were examined for visual changes of the fluids and materials, particulate formation, and film formation on the tube walls. The refrigerant portion of the sample was tested by gas chromatography-mass spectrometry (GC-MS) to identify and measure volatile components. The remaining lubricant portion was tested by titration to determine the lubricant acidity (Total Acid Number, or TAN), and by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) to quantify dissolved elements in the lubricants.

Evaluation of the sealed glass tubes after their prescribed aging but prior to opening revealed no significant visual differences between the refrigerants and conditions tested. As shown in Image 1, all liquids remained clear with no significant changes beyond slight discoloration observed. No film formation was observed on any of the tube walls, nor was there indication of notable precipitate formation.

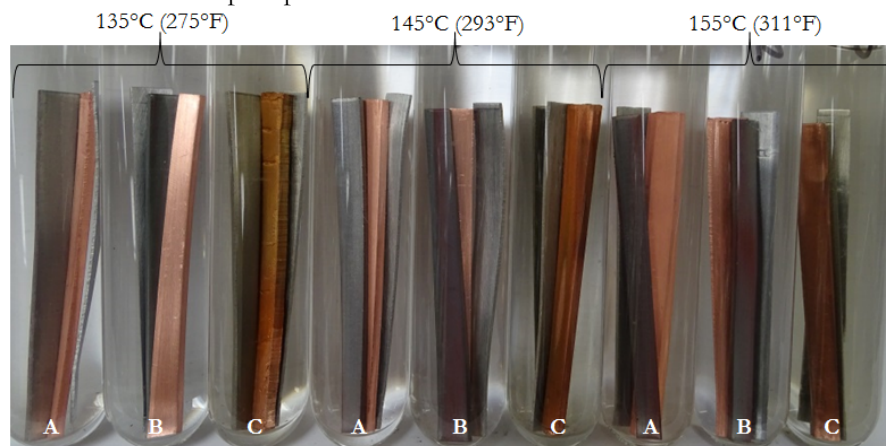


Image 1. Post-exposure photograph of sealed glass tube samples. ‘A’ corresponds to R-123 + mineral oil, ‘B’ corresponds to R-1233zd(E) + mineral oil, and ‘C’ corresponds to R-514A + POE based oil.

Refrigerant Breakdown Analysis. The refrigerant chemical stability was studied using GC-MS to identify and measure volatile degradation products. This sensitive technique allows for the separation and identification of volatile species, as well as semi-quantitation of components at or above 0.001% total peak area (10 ppm). Samples are analyzed by flashing the refrigerant from a refrigerant/lubricant mixture in a glass bulb, and introducing the vapor to the GC-MS for separation and analysis. Specific degradants of interest were measured, and the results are summarized in Table 2.

Table 2. Refrigerant Volatile Decomposition Products Measured by GC-MS from the Accelerated Reaction Study

Refrigerant Exposed	Decomposition Product(s)	Exposure Temperature (1 week)		
		135°C	145°C	155°C
R-123	R-133a	1480 ppm	2220 ppm	4230 ppm
R-1233zd(E)	R-1233zd(Z)	210 ppm	230 ppm	260 ppm
R-514A	R-1336mzz(E) + R-1130(Z)	440 ppm	400 ppm	630 ppm

Lubricant Evaluation. For all conditions and lubricants evaluated, TAN values were determined to be <0.1 mg KOH/g oil, and dissolved aluminum, copper, and iron concentrations were <10 ppm.

Contaminant Study

To evaluate the impact of system contaminants on the chemical stability of R-514A relative to R-123, a contaminant study was conducted. The contaminants included copper oxide, iron oxide, and iron chloride, with and without air and water present. Sealed glass tube samples were prepared with 50% refrigerant/50% lubricant by weight and included the contaminants of interest at 0.1% by weight based on the mass of refrigerant and lubricant used. In the tubes that included air and water, air was maintained at 1% and water was at 200 ppm. It was noted that iron chloride has a much higher solubility in the POE based lubricant used with R-514A than the mineral oil lubricant used with R-123 (Image 2). Anhydrous iron chloride is acidic in nature; therefore, as its lubricant solubility increases so will the corresponding lubricant TAN values (even prior to exposure).

Samples were exposed at 127°C (261°F) for one week. Post-exposure sample evaluations were similar to those described for the accelerated reaction study. Table 3 is a summary of the measured volatile refrigerant degradation products and lubricant acidities.

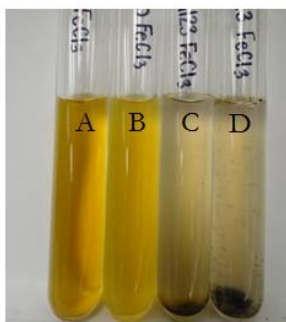


Image 2. Pre-exposure photograph of sealed glass tube samples containing 0.1% anhydrous iron chloride. ‘A’ and ‘B’ correspond to R-514A + POE based lubricant and ‘C’ and ‘D’ correspond to R-123 + mineral oil. Samples ‘B’ and ‘D’ contain 1% air and 200 ppm water, in addition to iron chloride.

Table 3. Refrigerant Volatile Decomposition Products Measured by GC-MS from the Contaminant Study

Contaminant(s)	Refrigerant Decomposition		Lubricant Acidity (mg KOH/g)	
	R-133a (R-123)	R-1336mzz(E) + R-1130(Z) (R-514A)	Mineral Oil (R-123)	POE based (R-514A)
Copper Oxide	554 ppm	348 ppm	<0.05	0.06
Copper Oxide + Water & Air	774 ppm	278 ppm	<0.05	0.08
Iron Oxide	1529 ppm	299 ppm	0.05	0.03
Iron Oxide + Water & Air	1082 ppm	369 ppm	<0.05	0.30
Iron Chloride	763 ppm	389 ppm	0.19	2.29
Iron Chloride + Water & Air	413 ppm	382 ppm	0.28	3.67

SYSTEM TESTING

Chiller Test Overview

Chemical stability assessments of R-514A were conducted during three separate chiller tests on two operating chillers. One of the chiller tests was specifically carried out with the intent to raise the refrigerant temperature to accelerate potential chemical reactions, and the other two tests were conducted at an endurance condition following performance and reliability assessments of the chillers. As summarized in Table 4, the chemical stability of R-514A was monitored over a combined chiller run time exceeding 3000 hours.

Table 4. Endurance Conditions for Refrigerant Testing

System/Test	Evaporator (T _{sat})	Condenser (T _{sat})	Chiller Hours in Endurance Mode	Total Chiller Hours
Chiller #1/Test #1	70°F (21°C)	115°F (46°C)	1400 hrs	1447 hrs
Chiller #2/Test #2	75°F (24°C)	113°F (45°C)	368 hrs	796 hrs
Chiller #1/Test #3	75°F (24°C)	118°F (48°C)	845 hrs	880 hrs

Image 3 is a photograph of one of the chillers tested in this study. Liquid refrigerant samples were collected from the evaporator and condenser of the systems at an average interval of every 100 hours. Lubricant samples were also acquired from the oil sump. Each liquid refrigerant sample was analyzed for purity, blend composition, moisture, acidity, and circulating lubricant content. Lubricant samples were analyzed for moisture, TAN, and dissolved elements.

Refrigerant Evaluation. Over the course of all testing, no significant changes were noted in the refrigerant chemistry, and no degradation of either blend component was detected. The measured impurities, degradants, and acidities all remained low for the duration of testing. Some residual R-123 (<1%) was present in the systems due to R-123 baseline testing conducted on the same chillers prior to the R-514A tests. However, the impurities other than R-123 remained below 0.1%, and no increases in degradation products were measured. Refrigerant acidity values did not increase above the detection limit of 1 ppm (as HCl). Moisture measured over the course of all tests was on average <30 ppm H₂O, and oil circulation rates from the evaporator and condenser refrigerant samples were consistent with expectations (<0.01% by weight in the condenser and <0.5% by weight in the evaporator).

In addition to the low pressure refrigerant assessments noted above, the blend composition of R-514A was evaluated by gas chromatography for all samples. Over the duration of all three chiller tests, the refrigerant blend composition was stable throughout the test period. The representative plot in Figure 1 illustrates the physical and chemical stability of R-514A demonstrated by the consistency in the measured R-1130(E) concentrations throughout the test period.



Image 3. One of two test chillers used to evaluate the performance and stability of R-514A.

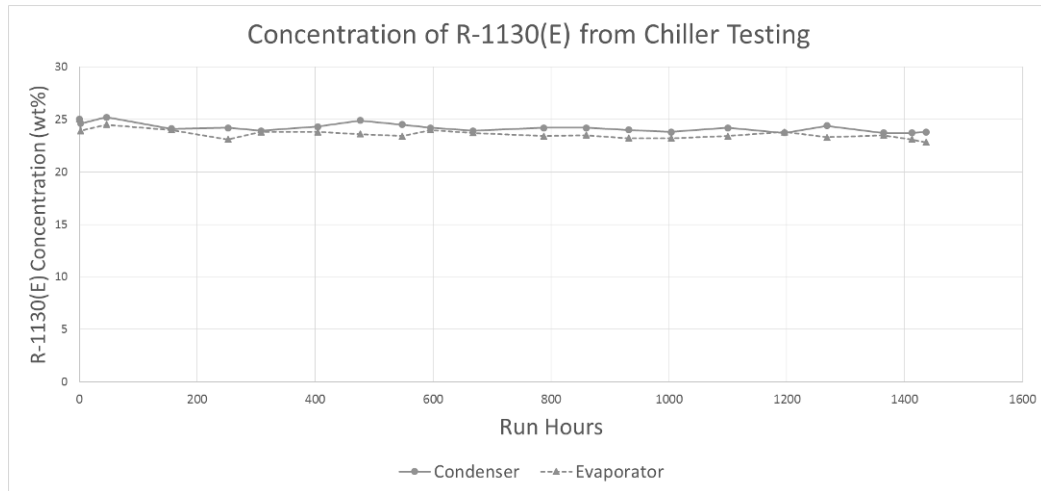


Figure 1. R-514A blend composition from chiller test #1 throughout >1400 hours of endurance testing.

Lubricant Evaluation. Over the course of each system test, no significant changes were noted in the TAN levels, with lubricant acidities remaining below 0.1 mg KOH/gram of oil. In chiller test #1, lubricant moisture concentrations were initially measured at levels near 130 ppm, but as the system equilibrated, moisture concentrations dropped and stabilized near 60 ppm. For chiller tests #2 and #3, lubricant moisture concentrations remained below 35 ppm throughout the test period.

Dissolved element concentrations varied by chiller. The chiller utilized in test #2 was a new production chiller, and all dissolved elements remained at concentrations <10 ppm throughout the study. The chiller utilized in tests #1 and #3 had been run with R-123 for many years. Lubricant samples from this chiller demonstrated dissolved elements such as iron, copper, and zinc at concentrations in the range of 10-20 ppm, as well as low single ppm concentrations of other dissolved elements. This is likely due to the the different solubility characteristics of the polar POE based lubricant relative to the nonpolar mineral oil lubricant which had been previously applied in the system. The propensity for POE based lubricants to liberate residues from systems previously applied with mineral oil is acknowledged in the industry, and is reviewed in Chapter 7 of the ASHRAE Refrigeration handbook (ASHRAE 2014).

DISCUSSION

During the accelerated reaction study, the observed R-123 degradation was much lower than predicted (0.1% - 0.4% measured vs. 0.5% - 3.0% predicted) based on external and internal chemical stability results from the early 1990s. One contributor to this difference is likely the lower R-123a isomer concentration in R-123 today (1-2%) versus concentrations in the original studies (>5%), as a result of improvements in refrigerant manufacturing and purification processes. Other potential contributors include the use of a different lubricant and different materials of construction in this study than those used in the original studies. Because the refrigerant, lubricant, and materials of construction used in this study are the same as those used in R-123 production chillers, these results best represent chemical stability of R-123 in systems as they are manufactured and applied today.

Relative to R-123 and mineral oil, results from the accelerated reaction study indicate that R-1233zd(E) and R-514A have less degradation at the same temperatures and under the same conditions. R-123 demonstrated decomposition of approximately 0.4% at 155°C, while R-1233zd(E) and R-514A both exhibited less than 0.1% degradation under the same conditions. These results support that the transition from R-123 to R-1233zd(E) or R-514A is low risk from a chemical stability perspective.

In some cases, the degradation products from olefin refrigerants have higher normal boiling points (lower vapor

pressure) than the refrigerant components. For instance, the R-1233zd(Z) degradation product is lower pressure than R-1233zd(E). For R-514A, two primary degradation products were measured – R-1336mzz(E) and R-1130(Z). R-1130(Z) is also a lower pressure chemical than either component of R-514A. It is important to note that analytical procedures must be in place to detect and measure lower pressure products that could be formed from olefin decomposition.

Results from the contaminant study demonstrated that R-514A had better chemical stability than R-123 in the presence of lubricants and contaminants including copper oxide, iron oxide, and iron chloride. Differences in the solubility of iron chloride in the polar and nonpolar lubricants resulted in increases in TAN values for the polar POE based lubricant relative to the nonpolar mineral oil lubricant; these changes are due to increases in contaminant solubility, not reactivity.

Results and trending analyses from refrigerant and lubricant tests from systems operating at worst-case and nominal conditions with R-514A confirm that the refrigerant and lubricant are chemically and physically stable. When converting from an HCFC refrigerant such as R-123 and mineral oil, it's possible that the new fluids will dissolve previously insoluble residues from the system. This is not a new industry phenomenon, and has been addressed previously during conversions from R-12 to R-134a, as well as other HCFC to HFC refrigerant transitions.

CONCLUSION

As the HVACR industry evaluates new refrigerant alternatives, a logical, application-focused approach should be used to assess the feasibility of new fluid chemistries. Using this approach, R-1233zd(E) and mineral oil, and R-514A and POE based lubricant, were demonstrated to exhibit better chemical stability than R-123 and mineral oil in sealed glass tube tests. Subsequent sealed glass tube tests with contaminants, and chemical stability monitoring of operating systems, confirmed the suitability of R-514A and POE based lubricant for use in low pressure centrifugal chiller systems initially designed for use with R-123. R-1233zd(E) was qualified for use in new centrifugal chiller equipment designs.

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