

Appendix A:

Draft Rule 6-5: Fluidized Catalytic Cracking Units (FCCUs)

Rules to Be Amended or Drafted

Regulation of emissions from fluidized catalytic cracking units requires drafting a new regulation: Regulation 6, Rule 5, *Particulate Emissions from Refinery Fluidized Catalytic Cracking Units* (Rule 6-5).

Goals

The goal of this rulemaking is to achieve technically feasible and cost-effective emission reductions of PM_{2.5} and PM_{2.5} precursors from fluidized catalytic cracking units (FCCUs) at Bay Area refineries. (PM_{2.5} is fine particulate matter with a diameter smaller than 2.5 microns.) The Air District plans to achieve emission reductions with two actions, as described in the “Workshop Report for the Refinery Emissions Reduction Strategy.” The first action will propose a new regulation that will address ammonia emissions (a PM_{2.5} precursor) at those FCCUs that use ammonia or urea injection. The second action will amend Regulation 6, Rule 5, to address both primary PM_{2.5} emissions and emissions of other PM_{2.5} precursors.

Background

Fluidized catalytic cracking units are complex processing units at refineries that convert heavy components of crude oil into light, high-octane products required in the production of gasoline.

The FCCU is so named because the catalyst comes in such small particles that it flows like a fluid. During the reaction phase, the catalyst becomes coated with petroleum coke, which must be burned off in the catalyst regenerator so that the catalyst can be reused. The catalyst regenerator exhaust contains particulate matter (PM), sulfur dioxide (SO₂), ammonia, carbon monoxide (CO), oxides of nitrogen (NO_x), and volatile organic compounds (VOC).

The Bay Area has five petroleum refineries. Four of these refineries—Chevron, Shell, Tesoro, and Valero—operate FCCUs. The Valero refinery recently has retrofitted its FCCU with a wet scrubber and its FCCUs have lower PM_{2.5} and SO₂ emissions than those at other refineries as a result. The Chevron and Tesoro FCCUs use ammonia to control filterable particulate matter emissions, which results in unreacted ammonia being emitted to the atmosphere (“ammonia slip”). The Shell FCCU uses ammonia or urea injection to control NO_x emissions, which results in unreacted ammonia being emitted to the atmosphere.

Process and Source Description

An FCCU consists of two vessels. (See Figure A1.) In the reactor vessel, the conversion reaction occurs in the presence of a fine, powdered catalyst and steam. During the conversion reaction the catalyst becomes coated with petroleum coke. In the regenerator vessel, this coke is removed from the surface of the spent catalyst by burning it off in the presence of air so that the catalyst can be reused. The cracked products from the reactor vessel are separated in a fractionator column into intermediate streams for further processing.

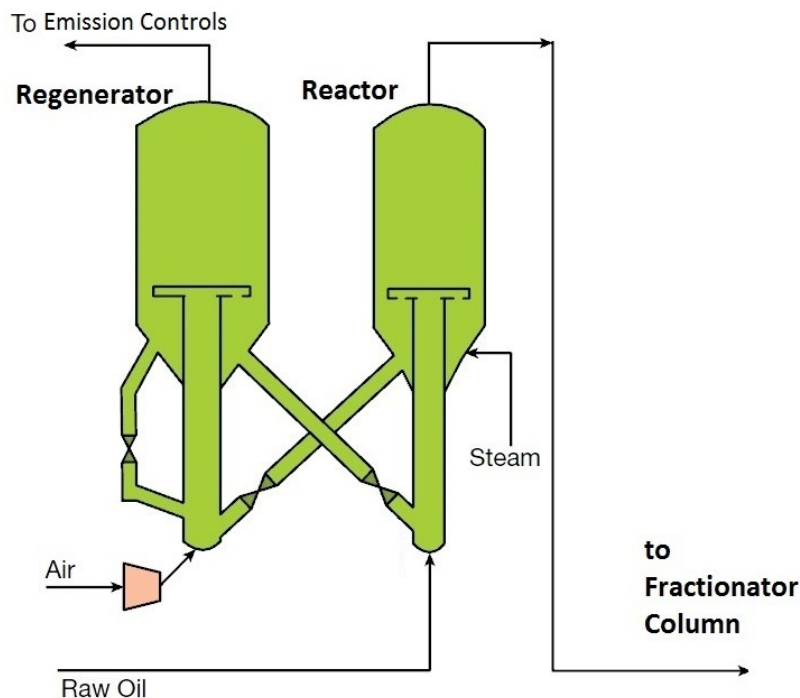


Figure A1: FCCU Process

The catalyst regenerator exhaust is the main emission point for the FCCU, which can emit high levels of PM, SO₂, ammonia, CO, NO_x, and VOC.

FCCU PM emissions can be classified as primary or secondary PM emissions. Secondary PM emissions are not particulate matter when emitted, but are precursors to the atmospheric formation of PM_{2.5}. Primary emissions may be further classified as material that is a liquid or solid at the emission point to the atmosphere (“filterable” particulate), or as material that is a gas at the emission point, but that immediately condenses in the atmosphere to a liquid or solid form (“condensable” particulate). This distinction is important because, until recently, particulate emissions from FCCUs were measured in the exhaust stack by collecting a sample from the exhaust stream at the stack—thus ignoring the condensable emission fraction. The most recent particulate test method developed accurately incorporates a condensation step to quantify condensable emissions. Limited source testing using this test method suggests that the amount of condensable particulate may be greater than the filterable amount in some FCCUs.

SO₂, ammonia, NO_x, and VOC can react in the atmosphere to form secondary PM_{2.5}. Most of the secondary PM_{2.5} formed in the Bay Area consists of ammonium sulfate and ammonium nitrate particles formed by reactions between ammonia and NO_x and SO₂ in humid air.

Because the FCCU exhaust contains so many pollutant species, a combination of emission control techniques often are utilized in FCCUs—typically flue gas additives to control NO_x and SO₂ and an electrostatic precipitator (ESP) to control PM. Bay Area refineries also use selective catalytic reduction (SCR) for NO_x control and wet scrubbers for control of multiple pollutants.

Regulatory History and Context

There currently are no Air District regulations that apply to ammonia emissions from FCCUs. There are two federal standards in 40 CFR part 60 that may apply to FCCUs, depending on the year of construction, reconstruction, or modification, but neither one applies limits to ammonia emissions.¹

Emissions

Based on recent source tests, ammonia concentrations at the FCCU catalyst regeneration outlet (post-control) are 29 parts per million by volume (ppmv) at the Chevron refinery and 23 ppmv at the Shell refinery. Test data are not available for the Tesoro refinery, but Tesoro is permitted to inject twice as much ammonia as the Chevron refinery actually uses.

Regulatory Concepts and Proposed Regulations

In 2003, South Coast Air Quality Management District (AQMD) adopted an ammonia emission limit of 10 ppmv, corrected to 3 percent oxygen, for FCCUs in its Rule 1105.1. The Bay Area Air District staff is proposing the same limit in Regulation 6, Rule 5. Air District staff also is proposing a continuous emission monitoring system (CEMS), whereas South Coast AQMD requires annual source tests. An emission limit of 10 ppmv recently was imposed at the Bay Area Valero refinery FCCU in an Air District permit, and this appears to be the most stringent emission limit imposed on refinery FCCUs.

Although Air District staff is proposing a stringent ammonia emission limit, it recognizes that ammonia and urea injections are used to promote PM control at FCCUs with electrostatic precipitators (ESPs) and that these ESPs are subject to Air District and federal PM emission limits. Therefore, although the Air District staff intends to impose the lowest possible ammonia emission limit for existing FCCUs, it will consider existing PM emission limits at the FCCU ESPs and the possible impact on ESP efficiency before proposing a final ammonia emission limit that will result in the greatest overall public health benefit.

Air District staff is proposing a limited exemption from the ammonia slip limits during startup and shutdown periods.

The proposed FCCU ammonia slip limit is 10 ppmvd, dry (ppmvd), corrected to 3 percent O₂, as a daily average. As an alternative, an affected refinery could instead reduce the overall emissions of primary PM from the FCCU by at least 50%. The value of the limit (10 ppmvd) is the same that appears in the recently amended Valero refinery FCCU permit and in South Coast Rule 1105.1 ("PM₁₀ and Ammonia Emissions from FCCUs," 2003). Based on source test data, the Chevron refinery operates significantly higher than this limit, because of high ammonia injection upstream of the FCCU ESP, as does the Shell refinery, because of urea injection to control NO_x emissions from the CO boilers that operate downstream of the FCCU. No ammonia source test data are available for Tesoro; but Tesoro is permitted to inject twice as much ammonia as the Chevron refinery actually uses.

Control Mechanisms

Source test data suggests that affected FCCUs can comply with PM emission limits from associated ESPs at significantly lower ammonia emission rates. It expects that the refineries that use ammonia or urea injection will be able to meet the proposed limits by optimizing injection locations and rates.

Costs and Emissions Reductions

¹ 40 CFR part 60, subpart J, *Standards of Performance for Petroleum Refineries*, and 40 CFR part 60, subpart Ja, *Standards of Performance for Petroleum Refineries for which Construction, Reconstruction, or Modification Commenced after May 14, 2007*.

Although there will be one-time optimization costs, reduced use of ammonia and urea should result in long-term cost savings.

Emission reductions are based on current emission rates of 29 ppmv (Chevron) and 23 ppmv (Shell) being reduced to 10 ppmv, then the resulting percentage reduction being applied to the associated mass emissions of ammonia at each refinery. Because of a lack of test data, the Tesoro emission reduction is assumed to be the same as at Shell. (See Table A1.)

Table A1: Affected Bay Area Refineries

Facility	Ammonia Reduction (tpy)	Capital Cost (\$ M)	Total Annualized Cost (\$ M)
Chevron	58	NA	NA
Shell	15	NA	NA
Tesoro	15*	NA	NA

*Assumed to be the same as Shell refinery from reduced use of ammonia injection.

Stakeholder Comments and Staff Responses

On May 26, 2015, Air District staff published a Request for Comments to solicit comments on the initial regulatory concepts that compose Phase 1 of the Refinery Emission Reduction Strategy. This request package included an earlier version of the concept papers for this draft rule.

Air District staff received two comment letters dated June 19, 2015, on this draft rule and associated concept paper. The commenters were:

1. Greg Karras et al., Citizens for a Better Environment (CBE); and
2. Guy Bjerke, Western States Petroleum Association (WSPA).

Staff’s responses to these comments are shown below.

Comment: *[Phased Approach:] We oppose delaying and piecemealing the FCCU rule. This piecemealing and delay is not supported by the vague assertion that “additional time and resources” are needed “to gather and confirm requisite information.” Please develop and propose the FCCU emission reduction Rule 6-5 as a whole instead of piecemealing it in phases, and please plan this urgently needed proposal as soon as possible, and if possible, in 2015. (CBE)*

Comment: *Four of the five Bay Area refiners operate FCCUs. District Staff says its proposal could reduce emissions from Chevron’s, Shell’s, and Tesoro’s FCCUs. It states that these three refiners inject ammonia or urea into their FCCUs’ electrostatic precipitators, and this increases their ammonia and PM_{2.5} emissions. We urge four changes to the scope of District Staff’s FCCU rule proposal:*

- *Please develop and propose this rule as a whole instead of piecemealing it, and please seek to propose it for consideration as soon as possible.*
- *Please consider prohibiting ammonia injection to electrostatic precipitators (ESPs).*
- *Please set limits that require process controls achieving the reduced FCCU emission levels already achieved by the installed, operational system at the Benicia refinery.*
- *Please limit FCCU mass emissions rate, coke-burn rate, or both, to prevent increased emissions that could be caused by foreseeable changes in refinery crude feedstock. (CBE)*

Staff Response: Staff appreciates the desire to expedite rule development for this rule. This desire for emissions reductions is the primary reason for bifurcating this effort. Achieving PM_{2.5} emissions via the first phase would require little to no additional control equipment as stated above. Adopting the measures in this phase would result in PM_{2.5} emissions reductions much earlier than if staff were to wait and develop these measures in a single effort. After the refineries have minimized overall PM_{2.5} emissions from their existing equipment, Air District staff will be able to determine whether additional PM_{2.5} controls are feasible. That evaluation of additional controls would also consider what measures would be feasible to reduce SO₂ emissions. With respect to emission increases due to feedstock changes, Staff believes that the appropriate way to address this issue is through changes to the permitting regulations to ensure that these impacts are reviewed prior to the refineries processing significantly different crude oil.

Comment: *The statement on page A:4 that “The Air District staff does not believe that the proposed [FCCU] regulations will require any additional controls. It expects that the refineries that use ammonia or urea injection will be able to meet the proposed limits by optimizing injection locations and rates.” As we have identified previously, refineries are all different; the fact that one refinery can meet the limit is insufficient evidence for assuming that all of them can. Based on the refineries’ operating experience, at least one refinery completely disagrees with staff’s assessment and others believe that staff does not have sufficient information to be able to assert this with confidence. (WSPA)*

Staff Response: District staff intends to meet with the owners/operators of each of the refineries to learn the specific obstacles to reducing ammonia addition at FCCUs. We will consider the information gathered from these meetings.

Comment: *The concept paper acknowledges that an exemption is needed for periods of startup, shutdown, bypass, or emergency bypass, but identifies that “because these definitions are always contentious,” the exemption will only be provided when a Permit to Operate explicitly provides it. WSPA strongly objects to this, and members have had negative experiences with these types of dependent actions in the past; if the exemption is needed, the rule ought to identify when it is needed (as the District has done in Rule 9-10), rather than creating a potentially unworkable situation down the road. (WSPA)*

Staff Response: District staff will include exemption criteria in the next draft of the rule.

Comment: *The statement in Section 6-5-101 of the draft language that “commingled emissions from an FCCU and one or more other sources from a single exhaust point shall all be considered to be FCCU emissions” is problematic, depending on the sources that are commingled; the limited exemption in 6-5-111 should also be clarified so that it applies to both the FCCU itself and any commingled sources. (WSPA)*

Staff Response: This statement is intended to make the rule provisions enforceable by establishing a presumption that all FCCU regenerator emissions are subject to the rule limits. District will consider any specific situations or circumstances that would make this presumption inappropriate. Also, the exemption in Section 6-5-111 is intended to apply to all emissions that are otherwise subject to rule limits during non-exempt periods; this exemption appears to achieve this intent.

Comment: *[Description of PM:] The following statements on page A:2 do not readily distinguish between what the District seems to be calling “indirect” and “direct” PM emissions:*

“Indirect PM emissions are not particulate matter when emitted, but are precursors to the atmospheric formation of PM_{2.5}. Direct emissions may be...material that is a gas at the emission point, but that immediately condenses in the atmosphere to a liquid or solid form (“condensable” particulate).”

To minimize confusion, it is suggested that the District use the federal terminology. It is misleading to call SO₂ and ammonia “indirect particulate” because not all of the emissions are converted to particulate; as the District is aware, these pollutants exist as gases in the air as well. (WSPA)

Staff Response: The next draft of the rule will incorporate the federal terminology.

**REGULATION 6
PARTICULATE MATTER
RULE 5
~~CONDENSABLE AND INDIRECT~~ PARTICULATE EMISSIONS FROM
REFINERY FLUIDIZED CATALYTIC CRACKING UNITS
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REGULATION 6
PARTICULATE MATTER
RULE 5
~~CONDENSABLE AND INDIRECT~~ PARTICULATE EMISSIONS FROM
REFINERY FLUIDIZED CATALYTIC CRACKING UNITS
(Adopted [Adoption Date])

6-5-100 GENERAL

6-5-101 Description: This rule limits the emissions of condensable ~~and indirect~~ particulate matter emissions from petroleum refinery fluidized catalytic cracking units (FCCUs), as well as emissions of precursors of secondary particulate matter. Regulation 6, Rule 1 addresses filterable particulate emissions from FCCUs. For the purposes of this rule, commingled emissions from an FCCU and one or more other sources from a single exhaust point shall all be considered to be FCCU emissions.

6-5-110 EXEMPTIONS

6-5-111 Limited Exemption, Emissions Abated by Wet Scrubber: The emission limit for ammonia in Section 6-5-301 shall not apply to emissions that are abated by a wet scrubber that is required to be operated by a District permit and that constitutes BACT for any pollutant.

6-5-112 Limited Exemption, Emissions during Startup or Shutdown Periods, ~~Bypass and Emergency Bypass:~~ The requirements of Section 6-5-301 shall not apply to emissions during an FCCU startup or shutdown periods, ~~bypass or emergency bypass period as specifically defined and allowed in a District Permit to Operate. This exemption shall apply only to the pollutants specified in the District Permit to Operate.~~

6-5-113 Limited Exemption, Installation of Wet Scrubber: The emission limit effective date for ammonia in Section 6-5-301 may be extended to a later date specified in a District Authority to Construct for an existing FCCU to be controlled with a new wet scrubber, but may not be extended by more than 36 months.

6-5-114 Limited Exemption, FCCU without Nitrogen-Based Additives: The emission limit for ammonia in Section 6-5-301 shall not apply to an FCCU where no ammonia, urea or any other nitrogen-based reducing agent is introduced into the CRU flue gas.

6-5-115 Limited Exemption, Primary Particulate Matter Reduction: The ammonia emission limit in Section 6-5-301 shall not apply to the owner/operator of a refinery that implements a primary particulate matter reduction in accordance with Section 6-5-403.

6-5-200 DEFINITIONS

6-5-201~~2~~ Ammonia Slip: Ammonia slip is the amount of unreacted ammonia emitted to the atmosphere from the FCCU, regardless of the source of the ammonia.

6-5-202~~3~~ Catalyst Regeneration Unit (CRU): A catalyst regeneration unit regenerates spent FCCU catalyst by burning off the coke that has deposited on the catalyst surface. The resulting CRU flue gas is the primary emission source addressed by this rule.

6-5-203~~4~~ Condensable Particulate Matter: Liquid droplets that coalesce, or gaseous emissions that condense to form liquid or solid particles. These liquid and/or solid particles are identified as condensable organic or condensable inorganic particulate matter using EPA Test Method 202. ~~Material emitted to the atmosphere in a gaseous form that condenses and/or reacts to form a solid or liquid at testing conditions.~~

6-5-204~~1~~ Daily~~7-day~~ Rolling Average: The arithmetic mean of the measured ammonia emissions subject to ~~described in~~ Section 6-5-301 on any calendar day that the FCCU

~~operates in the most recent 7 calendar days of operation of the FCCU. Each calendar day initiates a new rolling average period.~~

6-5-205 Fluidized Catalytic Cracking Unit (FCCU): A fluidized catalytic cracking unit (FCCU) is a processing unit that converts heavy petroleum fractions, typically from crude oil distillation units, into lighter fuel intermediates by using a fine, powdered catalyst to promote a chemical reaction in which the heavy petroleum molecules are broken into smaller molecules. In addition to the cracking reactor, an FCCU includes a catalyst regeneration unit (CRU), ancillary equipment including blowers, and all equipment for controlling air pollutant emissions and recovering heat.

~~**6-5-206 Indirect Particulate Matter:** Material emitted to the atmosphere in a gaseous form that will not condense to a solid or liquid form at atmospheric temperature and pressure, but that may chemically react in the atmosphere into a solid or liquid form. For the purposes of this rule, indirect particulate shall include only sulfur dioxide (SO₂) and ammonia.~~

6-5-206⁷ Petroleum Refinery: An establishment that is located on one or more contiguous or adjacent properties, and under common control, and that processes crude oil to produce more usable products such as gasoline, diesel fuel, aviation fuel, lubricating oils, asphalt or petrochemical feedstocks. Petroleum refinery processes include separation processes (e.g., atmospheric or vacuum distillation, and light ends recovery), petroleum conversion processes (e.g., cracking, reforming, alkylation, polymerization, isomerization, coking, and visbreaking) petroleum treating processes (e.g., hydrodesulfurization, hydrotreating, chemical sweetening, acid gas removal, and deasphalting), feedstock and product handling (e.g., storage, blending, loading, and unloading), and auxiliary facilities (e.g., boilers, waste water treatment, hydrogen production, sulfur recovery plant, cooling towers, blowdown systems, compressor engines, and power plants).

6-5-207 Primary Particulate Matter: Material emitted to the atmosphere as filterable or condensable particulate matter.

6-5-208 Secondary Particulate Matter: Material emitted to the atmosphere in a gaseous form that will not coalesce or condense to a solid or liquid form at atmospheric temperature and pressure, but that may react in the atmosphere into a solid or liquid form. For the purposes of this rule, precursors of Secondary Particulate Matter shall include sulfur dioxide (SO₂) and ammonia.

6-5-209 Startup and Shutdown Periods: Unless otherwise specified in a District Permit to Operate, FCCU startup is a period not exceeding 120 hours which begins with the startup of the main blower for introduction of catalyst and ends when fresh feed is introduced to the FCCU reactor and the process reaches steady state. Unless otherwise specified in a District Permit to Operate, FCCU shutdown is a period which begins when fresh feed is pulled from the FCCU reactor and ends when the main blower for catalyst recirculation is shutdown.

6-5-2010⁸ Wet Scrubber: A device that removes air pollutants from gas streams by contacting the gas stream with a scrubbing liquid.

6-5-300 STANDARDS

6-5-301 Fluidized Catalytic Cracking Unit (FCCU) Emission Limits: ~~A person operating~~The owner/operator of a Petroleum Refinery that includes an FCCU shall not cause emissions to the atmosphere from the FCCU that exceed the limits in Table 1 on or after the indicated effectiveness date:

Table 1 – FCCU Emission Limits		
Pollutant	Emission Limit	Effective Date
Ammonia	10 ppmvd at 3% O ₂ as a daily day-rolling average	January 1, 2018
Condensable Particulate Matter	[future]	[future]
Sulfur Dioxide (SO ₂)	[future]	[future]

6-5-400 ADMINISTRATIVE REQUIREMENTS

6-5-401 Ammonia Control Plan and Permit Applications: No later than January 1, 2017, ~~a person~~the owner/operator of a Petroleum Refinery subject to the ammonia emission limit in Section 6-5-301 shall submit to the APCO a control plan detailing the measures, if any, to be taken in order to meet the requirements of Section 6-5-301, and also applications for all Authorities to Construct necessary for compliance with Section 6-5-301.

6-5-402 Ammonia Monitoring Plan: No later than January 1, 2017, the owner/operator of a Petroleum Refinery that includes an FCCU subject to the ammonia emission limit in Section 6-5-301 shall submit to the APCO a plan for the installation of a continuous ammonia monitoring system to perform monitoring as required by Section 6-5-501. This plan shall identify the proposed monitoring technique, monitoring equipment, installation details and installation schedule.

6-5-403 Primary Particulate Matter Reduction: As an alternative to compliance with the ammonia emission limit of Section 6-5-301, the owner/operator of a refinery may instead achieve a permanent and enforceable overall emission reduction of primary particulate matter of at least 50% from baseline levels, no later than the effective date of the ammonia emission limit in Table 1. In order to use this alternative, the refinery owner/operator shall submit to the APCO a complete District permit application no later than January 1, 2017 that shall include the following:

403.1 Establish the actual average baseline emissions of primary particulate matter at the FCCU during the 3-year period immediately preceding the date of the application through verifiable records.

403.2 Indicate the measures that will be used to achieve a 50 percent reduction in primary particulate matter emissions no later than the effective date of the ammonia emission limit in Table 1.

403.3 The result of the complete permit application will be a new permit condition to limit the total emissions of primary particulate matter from the FCCU to no more than 50% of the baseline level.

6-5-500 MONITORING AND RECORDS

6-5-501 Ammonia Monitoring: ~~A person who operates an FCCU~~ The owner/operator of a Petroleum Refinery that includes an FCCU subject to the ammonia emission limit in Section 6-5-301 shall, no later than January 1, 2018, operate all of the following;

501.1 Continuous emission monitors that comply with District Regulation 1, Section 522 to continuously measure:

1.1 Oxygen concentrations downstream of the addition point of ammonia, urea or any other nitrogen-based reducing agent into the emission stream; ~~and,~~

1.2 NOx concentrations either:

2.1 before and after ammonia injection Upstream and downstream of the addition point of ammonia, urea or any other nitrogen-based reducing agent into the emission stream, or;

~~2.2 NOx concentrations after ammonia injection~~ Downstream of the addition point of ammonia, urea or any other nitrogen-based reducing agent into the emission stream, with the capability to measure NOx and NOx plus ammonia to obtain ammonia by difference, or;

~~1.34 Other APCO approved~~ Any other ammonia emission monitoring system approved in writing by the APCO.

501.2 Parametric monitors that comply with District Regulation 1, Section 523 to continuously measure the injection or addition rate (pounds per hour) of ammonia, urea or any other nitrogen-based reducing agent into the emission stream.

6-5-502 Ammonia Records: ~~A person who operates an FCCU~~ The owner/operator of a Petroleum Refinery subject to the ammonia emission limit in Section 6-5-301 shall maintain records of the data required to be measured in Section 6-5-501. These records shall be kept for a period of at least five years and shall be made available to the APCO on request.

6-5-600 MANUAL OF PROCEDURES

6-5-601 Compliance Determination: All compliance determinations shall be made in the as-found operating condition. No compliance determinations shall be made during periods subject to the exemption in Section 6-5-112.

6-5-602 Determination of Ammonia and Oxygen: Determination of ammonia shall be by Regulation 1, Section 522 NOx monitors or other APCO approved ammonia monitoring system. Determination of oxygen shall be by Regulation 1, Section 522 oxygen monitor.