Combination Corrosion Coupon Testing Needed for Today's Control Equipment

Accurate reliability analyses for electronic/electrical devices in pulp and paper mills require silver and gold coupons in addition to copper

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INTRODUCTION

Copper, silver, and gold are important functional materials found in many of the electrical/electronic devices in use in today's pulp and paper mill control rooms. The reliability of these devices may be greatly affected by the presence of corrosive gases in the local environment. Even trace levels of these gases can cause failures due to the formation of corrosion products in and on the circuitry and connectors of these devices. And due to the nature of the processes involved in paper manufacturing, it is almost a certainty that these devices will at sometime be exposed to corrosive gases.

Atmospheric corrosion of copper has been studied extensively and tests have been devised to measure the rates of copper corrosion. These corrosion rates are currently being used to gauge electrical/electronic equipment reliability. The higher the rate of copper corrosion, the higher the probability of equipment damage and/or failure (due to corrosion).

Studies of both laboratory and field data collected by Purafil, Inc. has shown that using copper corrosion alone as a gauge for equipment reliability can seriously understate the corrosive potential of the local environment. Examination of both silver and gold corrosion data have shown instances of an environment which is noncorrosive to copper being extremely corrosive to silver and/or gold. It is because of results such as these that any testing which attempts to predict electrical/electronic equipment reliability should incorporate copper, silver, **and** gold corrosion as determinants.

CURRENT STANDARDS AND METHODOLOGIES

The Instrument Society of America (ISA) published a standard[1] with which to classify airborne contaminants that may affect process measurement and control systems. This presented the manufacturers and users of electrical/electronic devices a way to predict the reliability of those devices exposed to corrosive gases. One method involves the use of specially prepared copper coupons. These coupons are placed in the local operating environment for a period of time, usually thirty days, and then tested[2,3] for the amount of corrosion film build-up. This provides a means of specifying the type and concentration of gaseous contaminants to which equipment may have been exposed. The ISA classification of reactive environments for gaseous contaminants is shown in **Figure 1**.

FIGURE 1 - Classification of Reactive Environments

Severity Level			G1 Mild	G2 Moderate	G3 Harsh	GX Severe
Copper Reactivity Level (In angstroms)[a]			<300	<1000	<2000	≥2000
The gas concentration levels shown below are provided for reference purposes. They are believed to approximate the Copper Reactivity Levels stated above, providing the relative humidity is less than 50%. For a given gas concentration, the Severity Level (and Copper Reactivity Level) can be expected to be increased by one level for each 10% increase in relative humidity above 50% or for a humidity rate of change greater than 6% per hour.						
Gas Concentration[b]						
	Contaminant	Gas	Concentration			
Reactive Species[c,d]	Group A	H_2S	<3	<10	<50	≥50
		SO_2, SO_3	<10	<50	<300	≥300
		Cl_2	<1	<2	<10	≥10
		NO_X	<50	<125	<1250	≥1250
	Group B	HF	<1	<2	<10	≥10
		NH_3	<500	<10,000	<25,000	≥25,000
		O_3	<2	<25	<100	≥100

NOTES: a - Measured in angstroms after one month's exposure. See Reference #1, Appendix C, Item Numbers 2, 3.
b - mm^3/m^3 (cubic millimeters per cubic meter) parts per billion average for test period for the gases in Groups A and B.
c - The Group A contaminants often occur together and the reactivity levels include the synergistic effects of these contaminants.
d - The synergistic effects of Group B contaminants are not known at this time.

There are four severity levels in the standard; G1, G2, G3, and GX. Each level represents a more corrosive environment, decreasing equipment reliability, and the higher probability of corrosion-related failure than the one preceding it. The standard defines these contaminant severity levels as outlined below.

Severity Level G1: Mild - An environment sufficiently well-controlled that corrosion is not a factor in determining equipment reliability.
Severity Level G2: Moderate - An environment in which the effects of corrosion are measurable and may be a factor in determining equipment reliability.
Severity Level G3: Harsh - An environment in which there is a high probability that corrosive attack will occur. These harsh levels should prompt further evaluation resulting in environmental controls or specially designed and packaged equipment.
Severity Level GX: Severe - An environment in which only specially designed and packaged equipment would be expected to survive. Specifications for equipment in this class are a matter of negotiation between user and supplier.

Each Severity Level has a corresponding copper reactivity level which has a direct relation to the amount of corrosion film build-up (**Figure 1**). This build-up, or thickness, is measured in angstroms. In technical terms an angstrom (Å) is one ten-billionth of meter (39.37 inches). This is indeed a small number. To help visualize this distance, the following example is offered. (Assume the amount of rain to be equal to corrosion film thickness, the ability of the stack of papaw to remain standing as a measure of equipment reliability, and the stack of paper falling as equipment failure.)

Assume the thickness of a sheet of paper to be one angstrom. At 500 sheets per ream, one would need twenty million reams of paper to equal one meter. If a standard ream is assumed to be approximately two inches thick, this stack of paper would be over 630 miles tall! Assume the stack is stable and freestanding and will not fall unless the bottom of the stack becomes wet...and then come the rains!

With a **Mild** (G1) shower, the bottom 1¼ inches (300Å) of our stack could become wet without fear of the stack falling. A **Severe** (GX) storm would wet the bottom 8 inches (2000Å) of the stack and cause the entire stack to come tumbling down. Any amount of rain in between would cause the stack to begin to sway and the possibility of the stack falling would increase as the amount of rain increased. Therefore, to turn what was once a freestanding stack of paper over 630 miles tall into a tremendous pile of trash, only the bottom eight inches would need to become wet. Just as minuscule amounts of rain (relative to the height of the stack) could topple this stack, small amounts of corrosion build-up on electrical/electronic equipment could cause the shutdown of a pulp and paper mill due to equipment failure.

PURAFIL CORROSION CLASSIFICATION COUPONS

Purafil, Inc. has been performing corrosion testing for a number of years as a diagnostic tool in response to customers' needs and requests. During this time more than five thousand Corrosion Classification Coupons (CCC) have been analyzed with more than half of these being returned from pulp and paper mills. One difference these CCC's have from the ISA standard is that they employ both copper and silver coupons. Although silver is not a equipment reliability determinant in this standard, it was included because of independent studies citing silver being a better indicator of environmental chlorine than copper[4]. The use of these two types of coupons presented, on occasion, results that were quite surprising. Some environments that were non-corrosive to copper, and thus considered harmless to equipment (by the ISA standard), were extremely corrosive to silver. It was felt that using only the copper corrosion results from these CCC's would seriously understate the potential for equipment failure in these environments. It was becoming apparent that the standard being used to project the corrosive potential of an area was inadequate.

As mentioned in the introduction to this article, copper, silver, and gold are important functional materials found in electrical/ electronic devices. Gold especially is being used more and more in these devices because of its resistance to corrosive attack. Connectors on printed circuit boards, data transmission cables, etc., are being plated with a thin film of gold to prevent corrosion from occurring on these surfaces. These connectors are where corrosive attack is most likely to cause equipment failure. Although the gold itself does not corrode, the thin gold film is very porous and corrosive gases can attack the metal underneath through these pores. The corrosion film can then spread up to the surface of the gold layer and ultimately cause device failure. Purafil, Inc. has been offering CCC's with copper, silver, and gold coupons for more than a year. Similar inconsistencies as observed between copper and silver coupons have presented themselves upon examination of field-exposed gold coupons. Testing was proposed to see if similar results could be obtained in a controlled laboratory setting. It was hoped that the conditions under which the above occurred might be determined.

LABORATORY-EXPOSED CORROSION CLASSIFICATION COUPON TEST RESULTS

The ISA Standard defines corrosion in terms of the corrosion film thickness which builds up on specially prepared copper coupons after one month of exposure. It gives instructions for the preparation, exposure, and sample analysis of Copper Reactivity Samples. Because silver coupons were also used in this test, these same instructions were followed for the Silver Reactivity Samples. (The classification method for the gold coupons will be described later.) The basic premise of the test was to introduce known concentrations of gas(es) into environmentally controlled[1,5,6] chambers containing copper, silver, and gold coupons. Regression analyses were then performed on the results of the copper/silver corrosion. These analyses showed corrosion trends for each type of coupon as well as the effects of different gas combinations on each type of coupon[7]. The gold coupons were inspected for the presence or absence of pore corrosion.

Figure 1 lists two groups of gases designated as "Groups A and B". The Group A gases are those most frequently encountered in pulp and paper mills and include inorganic chlorine compounds (chlorine - Cl_2, chlorine dioxide - ClO_2, hydrogen chloride - HCl, etc.), active sulfur compounds (hydrogen sulfide - H_2S, sulfur - S, etc.), sulfur oxides (sulfur dioxide - SO_2, sulfur trioxide - SO_3), and nitrogen oxides (nitric oxide - NO, nitrogen dioxide - NO_2, nitrogen tetroxide - N_2O_4). The four gases which were used in this test were **chlorine**, **hydrogen sulfide**, **nitrogen dioxide**, and **sulfur dioxide**.

The results of the copper and silver corrosion film analyses were recorded as total corrosion film thickness. This follows the methodology of the ISA Standard. Results of the regression analyses performed on the data are presented in **Table 1** and used for the plots in **Figures 2-5**. Although gold pore corrosion was observed, the results were inconclusive and will not be reported here.

After plotting the regression values for all the results obtained in the test, one significant trend presented itself for the **COPPER COUPONS**. When H_2S is plotted along with the five combinations that contained this gas, all six lines fall almost on top of each other (**Figure 4**). This suggests that, for these four gases under the conditions of this test, **COPPER CORROSION** is dominated by H_2S. Chlorine without H_2S produces little corrosion as do combinations of Cl_2, NO_2, and SO_2. SO_2 even appears to reduce the corrosion on copper when present with these other gases. Under these test conditions, the magnitude of the H_2S-induced corrosion is greater than any observed synergistic effects of different gas combinations.

While these gas combinations did not show any appreciable synergy on the amount of copper corrosion, one combination did produce excessive corrosion over and above the expected levels on the **SILVER COUPONS**. Although H_2S and NO_2 were not particularly corrosive to the **SILVER**

COUPONS <u>by themselves, combining the two produced more than 4½ times the calculated expected silver corrosion levels.</u> All combinations which contained these two gases showed similar results and plots of the regression values very closely tracked the H_2S+NO_2 pair (**Figure 5**). This powerful synergy overshadows any corrosive effects from any of the other gases. Where these two gases were not in combination, the expected values closely matched the measured values.

FIGURE 2 - COPPER CORROSION

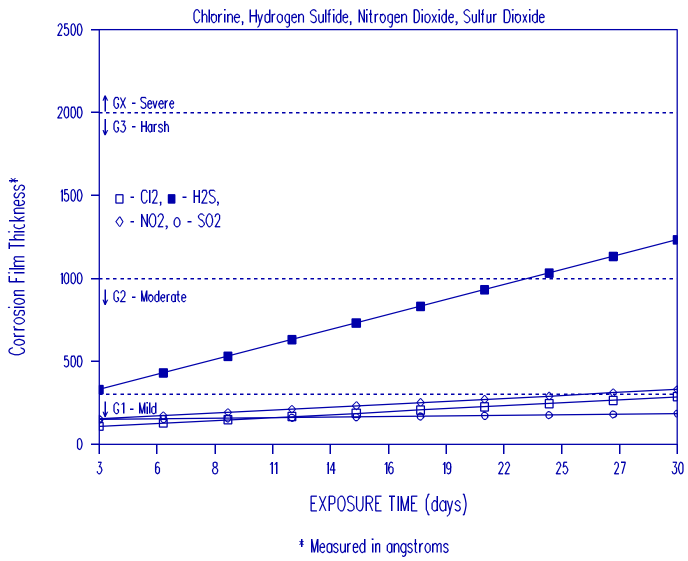


FIGURE 3 - SILVER CORROSION

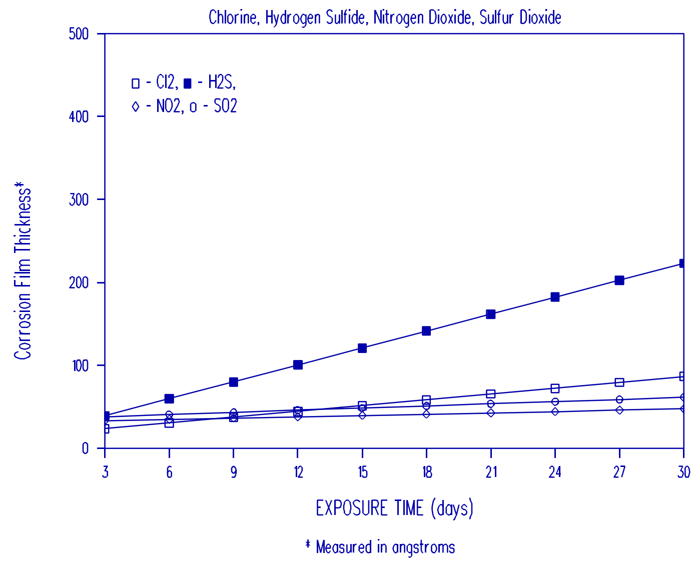


FIGURE 4 - COPPER CORROSION

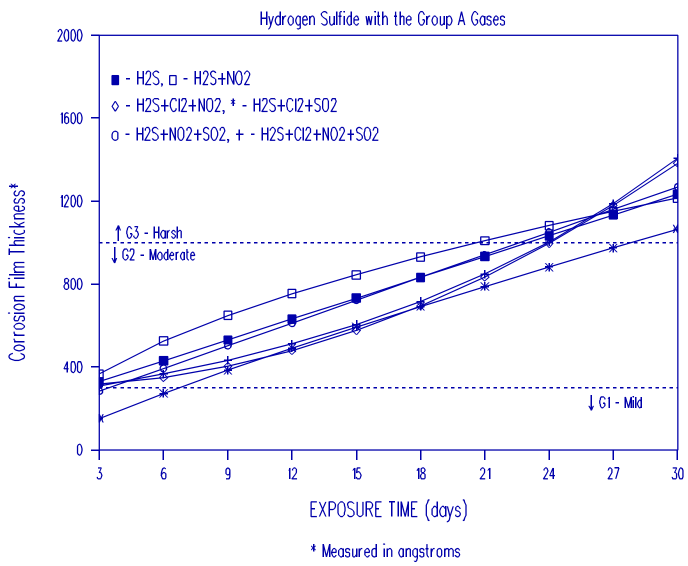
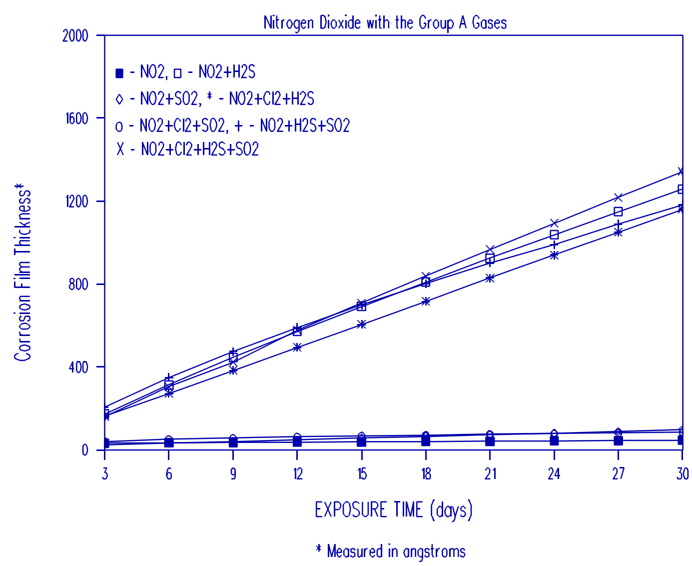


FIGURE 5 - SILVER CORROSION



The results of this testing indicate that for COPPER COUPONS the presence or absence of hydrogen sulfide (H_2S) and for SILVER COUPONS the presence or absence of hydrogen sulfide in combination with nitrogen dioxide (NO_2) had the most profound effect on the amount of corrosion produced. <u>This leads to an interpretation that the presence or absence of H_2S or H_2S+NO_2 when</u>

using **COPPER COUPONS** and **SILVER COUPONS** respectively would be the major factor in determining equipment reliability.

FIELD-EXPOSED CORROSION CLASSIFICATION COUPON TEST RESULTS

The inconsistencies that presented themselves between the copper and silver coupons led to concern over the true corrosive potential of some environments. These inconsistencies showed up in both laboratory and field exposed coupons. With these significant differences between copper and silver coupons, it was felt that the same may be true if gold coupons were included. Purafil, Inc. has offered Corrosion Classification Coupons (CCC's) for more than five years with an optional gold-plated coupon which shows how gold-plated contacts can be affected by the presence of corrosive gases. Since their introduction, over 4000 "gold CCC's" have been delivered to the field and more than 3800 have been returned to Purafil laboratories for analysis. The copper and silver coupons were analyzed as per the ISA standard. The gold coupons were evaluated as described below.

As stated above, the porous gold layer does not itself corrode. Rather, it is the corrosion of the metal underneath the gold (nickel in this case) that corrodes and it is these corrosion products that appear on the gold layer. This type of corrosion is known as pore corrosion. A microphotograph is taken of the gold coupon upon receipt and it is inspected for the presence or absence of pore corrosion. The amount of pore corrosion per unit area is used to determine the corrosive potential of the environment to which the coupon was exposed.

Representative data obtained for the "gold CCC's" returned from the field is shown in **Table 2** and includes results for the three types of coupons. These results have been sorted by increasing copper coupon corrosion - ISA classifications G1 through GX - to illustrate how an environment which is noncorrosive to copper can be highly corrosive to other metals. The copper and silver corrosion is presented as corrosion film thickness (in angstroms). The gold pore corrosion is presented as a severity scale ranging from 1 to 5 with **1** showing no pore corrosion and **5** showing the most severe pore corrosion.

Of the seven CCC's that were reported as ISA Class G1 - Mild, two (Nos. 1 and 3) showed significant silver corrosion and two (Nos.2 and 3) showed significant gold pore corrosion. One silver coupon (#9) and one gold coupon (#7) showed significant corrosion at the ISA Class G2 - Moderate level. Although there was one silver and gold coupon (#15) which showed higher corrosion at the ISA Class G3 - Harsh level, these rooms/areas are already compromised by the presence of high levels of corrosive gases and should be treated to prevent further damage from corrosion. Premature failure of any electrical/electronic equipment is almost certain otherwise.

It should be noted that currently there are no standards more widely used for the classification of corrosive environments other than the one cited. The use of silver and/or gold coupons in addition to the ISA standard's copper coupons can be used to get a more complete representation of the corrosive potential of an environment which contains electrical/electronic equipment. The money invested in this equipment and that which it controls makes it imperative that the most accurate determinations be made to protect these investments. This cannot be done by using copper coupons alone. All functional materials must be considered.

One question in interpreting results from field-exposed CCC's is that (usually) neither the exact contaminants and their concentrations nor the humidity and temperature of the local environment are known. With a standard developed only for copper coupons, silver and gold corrosion data must be interpreted carefully. The big advantage field-exposed coupons have over laboratory testing or any standard interpretation is that the corrosion produced is due to the same environment to which equipment is being exposed. This "real-time" picture of what is actually happening to these functional materials can be an invaluable tool in determining equipment reliability. These field results as well as some of the data which presented itself in the above laboratory testing presents a case for the inclusion of silver **and** gold corrosion for the determination of equipment reliability.

CONCLUSION

The reliability of electrical/electronic equipment in corrosive environments must be accurately gauged to avoid equipment failure. It has become apparent that using a standard which employs copper-only testing is inadequate for this purpose. Field-exposed Corrosion Classification Coupons (CCC's) have shown environments which would be considered noncorrosive by current (copper) standards can be extremely corrosive to other functional materials. This was observed first on CCC's with copper and silver coupons and, more recently, with copper, silver, and gold coupons. Laboratory testing has produced similar results and has shown how the presence or absence or certain corrosive gases affects the formation of corrosion on these metals.

The use of copper, silver, and gold coupons for assessing the corrosive potential of an environment gives a more complete picture of what is actually occurring in that environment. By using the results obtained from these CCC's, one can tell what type of contaminants were present and develop proper control strategies. The probability of electrical/electronic equipment failure due to corrosive attack can practically be eliminated by looking beyond copper-only environmental classifications.

REFERENCES

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3. W.E. Campbell and U.B. Thomas, "Tarnish Studies," Bell Telephone System Technical Publications, Monograph 13, 1170, 1939.
4. D.W. Rice, P. Peterson, E.B. Rigby, P.B.P. Phipps, R.J. Cappell, and R. Tremoureaux, Journal of the Electrochemical Society: Electrochemical Science and Technology, Vol. 128, No. 2, pp. 275-284, February, 1981.

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TABLE 1 - COPPER AND SILVER CORROSION (Regression Values)

Copper Coupon Test Data - Total Copper Corrosion

Coupon No.	Cl^2	H^2S	NO^2	SO^2	Cl^2, H^2S	Cl^2, SO^2	H^2S, NO^2	NO^2, SO^2	Cl^2,H^2S, NO^2	Cl_2, H^2S, SO^2	Cl^2, NO^2, SO^2	H^2S, NO^2, SO^2	Cl^2, H^2S, NO^2, SO_2
3	108	330	153	149	57	129	366	170	317	152	250	283	309
6	127	431	173	153	236	137	525	197	349	273	354	393	367
9	147	531	193	157	414	146	649	223	403	385	434	503	433
12	167	631	212	161	592	155	754	249	479	491	501	612	512
15	187	732	232	165	771	166	845	276	576	593	561	722	606
18	207	832	252	169	949	179	931	302	694	692	614	832	717
21	226	932	271	173	1127	194	1009	329	834	788	663	941	848
24	246	1033	291	176	1306	212	1082	355	996	882	709	1051	1004
27	266	1133	311	180	1484	233	1151	382	1179	975	752	1161	1188
30	286	1233	330	184	1662	259	1215	408	1384	1065	793	1270	1406
ISA*	***1000***	***1000***	***1000***	***450***	***2000***	***1450***	***2000***	***1450***	***3000***	***2450***	***2450***	***2450***	***3450***
(+/-)%	***-71%***	***23%***	***-67%***	***-59%***	***-17%***	***-82%***	***-39%***	***-72%***	***-54%***	***-57%***	***-68%***	***-48%***	***-59%***
		EXPECTED			***1480***	***431***	***1517***	***476***	***1730***	***1620***	***654***	***1566***	***1766***
		DIFFERENCE (+/-)%			***12%***	***-40%***	***-20%***	***-14%***	***-20%***	***-34%***	***21%***	***-19%***	***-20%***

Silver Coupon Test Data - Total Silver Corrosion

Coupon No.	Cl^2	H^2S	NO^2	SO^2	Cl^2, H^2S	Cl^2, SO^2	H^2S, NO^2	NO^2, SO^2	Cl^2,H^2S, NO^2	Cl_2, H^2S, SO^2	Cl^2, NO^2, SO^2	H^2S, NO^2, SO^2	Cl^2, H^2S, NO^2, SO_2
3	23	39	33	38	33	8	173	25	162	57	41	206	161
6	30	60	35	41	68	18	314	33	273	89	51	349	305
9	37	80	36	43	104	29	446	41	384	115	58	475	423
12	44	100	38	46	140	40	571	49	495	139	63	590	577
15	51	121	40	48	175	52	692	57	606	160	68	699	709
18	58	141	41	51	211	65	810	65	717	181	72	802	839
21	65	162	43	54	247	77	925	73	829	199	76	902	967
24	72	182	44	56	282	90	1038	81	940	217	79	990	1093
27	79	203	46	59	318	103	1149	89	1051	235	82	1091	1219
30	86	223	47	61	354	116	1258	97	1162	251	85	1181	1343
		EXPECTED			***309***	***148***	***270***	***109***	***547***	***307***	***118***	***507***	***527***
		DIFFERENCE (+/-)%			***14%***	***-21%***	***365%***	***-11%***	***112%***	***-18%***	***-28%***	***133%***	***155%***

TABLE 2 - Field-exposed CCC's

COPPER - SILVER - GOLD COUPON DATA
(Sorted by ISA Class & Copper Corrosion)

CCC #	CCC PANEL #	ISA CLASS	COPPER CORROSION	SILVER CORROSION	Ag/Cu RATIO	GOLD PORE CORROSION
1	3003	G1	151	***846***	***5.6026***	2
2	3004	G1	167	219	1.3114	***4***
3	8012	G1	186	***2468***	***13.269***	***4***
4	6001	G1	201	226	1.1244	1
5	5034	G1	216	95	0.4398	1
6	7003	G1	234	128	0.547	1
7	3002	G2	315	766	2.4317	***4***
8	4066	G2	320	285	0.8906	2
9	6000	G2	417	***1556***	***3.7314***	2
10	2005	G2	463	331	0.7149	2
11	6001	G2	470	935	1.9894	2
12	7015	G2	784	373	0.4758	3
13	7006	G2	791	590	0.7459	4
14	2605	G3	1096	1731	1.5794	2
15	1074	G3	1228	***2848***	***2.3192***	***4***
16	8000	G3	1243	598	0.4811	3
17	2603	G3	1349	1215	0.9007	2
18	6002	GX	2330	2897	1.2433	2
19	8010	GX	2845	1175	0.413	5
20	2602	GX	3308	4678	1.4141	5
21	4063	GX	3783	570	0.1507	5
22	6004	GX	3799	1523	0.4009	4
23	1055	GX	4278	3266	0.7634	2
24	1057	GX	4684	2221	0.4742	4
25	2409	GX	4912	1830	0.3726	1
26	2604	GX	4918	2160	0.4392	2
27	8086	GX	5372	2531	0.4711	5
28	4056	GX	7540	6075	0.8057	4
29	3001	GX	8533	3147	0.3688	5
30	2425	GX	11370	3191	0.2807	5
31	8011	GX	36244	10880	0.3002	5
32	4032	GX	51202	14047	0.2743	5
33	2006	GX	78656	12206	0.1552	5
34	8014	GX	80179	14920	0.1861	5
35	2016	GX	89275	22041	0.2469	5
36	8091	GX	102971	26850	0.2608	5
37	9070	GX	107666	12698	0.1179	5
38	1054	GX	109274	31894	0.2919	5
39	4057	GX	135060	14644	0.1084	5
40	9090	N/A	281	180	0.6406	1
41	9061	N/A	2019	980	0.4854	3